



# Modulated magnetic and structural states

Dynamics and functionalities

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## List of Publications

**Magnetic monopoles and toroidal moments in  $\text{LuFeO}_3$  and related compounds**

F. Foggetti, S. W. Cheong, S. Artyukhin, Phys. Rev. B 100, 180408(R), doi: 10.1103/PhysRevB.100.180408

**Soft magnon contributions to dielectric constant in spiral magnets with domain walls**

F. Foggetti, A. Pimenov, S. Artyukhin, arXiv:2012.15383

**Skyrmion signatures in the ultrafast time domain: coherent and incoherent photo-excited spin dynamics of Néel-type skyrmion host  $\text{GaV}_4\text{S}_8$**

F. Sekiguchi, F. Foggetti, S. Artyukhin, K. Budzinauskas, P. Padmanabhan, R. B. Versteeg, V. Tsurkan, I. Kézsmárki, P. H. M. van Loosdrecht, in preparation

**Improper ferroelectricity in metal-organic frameworks**

F. Foggetti, A. Stroppa, S. Artyukhin, in preparation

**Theory of Devil staircase in  $\text{IrTe}_2$**  F. Foggetti, D. Khomskii, S. Artyukhin, in preparation

**Motion of ferroelectric domain walls in spiral magnets**

F. Foggetti, S. Artyukhin, in preparation

**Magnetic excitations in  $\text{Ni}_3\text{TeO}_6$**

F. Foggetti, S. Artyukhin, in preparation



# Introduction

The study and comprehension of the properties of matter has been, and still is, a crucial topic in the development of our civilization. As the characteristics of different materials were revealed, new technologies were built, new phenomena were observed, and new discoveries were made. The knowledge that scientists of the past produced acted as a stepping stone for their successors, enabling them to continue studying and unraveling the hidden treasures that the nature keeps secret.

As the research continues, the possibilities for different materials keep increasing. For example, if we consider materials science, we observe a dramatic increase in the number of new materials created during the last century. We moved from the optimized use of the naturally available resources (i.e. metals, minerals, fuel...) to a situation in which we create new materials according to our needs. We can now construct something completely new, that behaves like nothing known before (2D and layered materials, new alloys, perovskites, organic-inorganic hybrid materials to name a few). As the number of new interesting materials grows, so does their inherent complexity, thus forcing new ways to describe them and new tools to address the problems that come with their study.

*Complexity* is a key word in this context. As the inner structures of the materials we are studying are becoming less and less trivial, the physics that they host becomes far more complex. As a double edged sword the complexity of a physical system prevents us from an easy description of the latter, but also hides new phenomena that have no analogues in simpler systems. We often refer to the appearing of new physics from a complex background as *emergence*. Examples of emergent physics are collective excitations inside materials (phonons, magnons and other quasi particles) as well as new, unobserved, phases and states of matter.

This Thesis is mainly, but not only, focused on the study of these kinds of excitations. Great importance is given in particular to magnetic excitations (magnons) that will be contextualized with the peculiar orders of the materials that exhibit them. The concept of order is of crucial importance, as the emergence of the properties we try to rationalize is directly caused by the particular order and structure of a material we examine. In this Thesis diverse problems have been reported. The structure of the Thesis is the following: each project has a dedicated Chapter and every Chapter has a brief introduction to make the reader accustomed to the different language, tools, and physical background of the case. The content of the chapters is summarized here:

- In Chapter 1 we study the magnetic excitations of a 2D triangular spin lattice, a structure that has been observed in materials such as hexagonal manganites and ferrites ( $\text{RMnO}_3$  and  $\text{RFeO}_3$  with R being a rare earth element). We consider the particular case of  $\text{LuFeO}_3$ , where many of the layers we describe are stacked on top of each other. We study the collective magnetic excitation (magnons) in the lattice in order to identify signatures of elusive magnetic order that this material can host, magnetic monopoles and toroidal moments.

- In Chapter 2 we further exploit the analytical tools developed in Chapter 1. We analyze magnetic and electric excitations in a spin chain where *magnetic frustration* induces a cycloidal arrangement of spins, a configuration observed in materials such as  $\text{TbMnO}_3$  and  $\text{MnWO}_4$ . We compute the contributions of the excitation to magnetic and electric susceptibilities and discuss how the excitations affect the dielectric properties of the material.
- In Chapter 3 we discuss the properties of the multiferroic  $\text{GaV}_4\text{S}_8$ . Starting from experimental evidences of magnon photoinduced dynamics and thermal transport we perform a simulation based on a realistic microscopic model. The model takes into account the fundamental symmetric (Heisenberg) and anti-symmetric (Dzyaloshinskii-Moriya) spin interactions as well as spin anisotropy and external magnetic field. A combination with LLG equation is used to describe the spin dynamics. This simple asset is sufficient to reproduce the rich phase diagram of the real material for different magnetic fields and temperatures as well as describing the physical behaviour of the coherent and incoherent dynamics of the magnon excitations. This set of tools is then used to address the problem of magnetic phase-dependent thermal conductivity and the photoinduced precession motion of the magnetization.
- In Chapter 4 we discuss a new mechanism for improper ferroelectricity in hybrid organic-inorganic materials. We study  $(\text{DMA})\text{Fe}^{II-III}(\text{COOH})_3$  (DMA being  $\text{NH}_2(\text{CH}_3)$ ) where a small ferroelectric polarization has been observed. We use a Landau theory to describe the phase transition that generates the polarization and we compute the phase diagram of the material. As the discovered mechanism is related to the toroidal ordering of DMA molecules and can be extended to other similar structures, we compute the energy barrier for the rotation of DMA molecules in our particular case.
- In Chapter 5 we discuss  $\text{IrTe}_2$ , a layered transition metal dichalcogenide that presents a series of stripe-ordered states. Stripes are formed by Ir dimers. Ir atoms dimerize by shortening their bond length by 20%, and dimers order in stripes throughout the material. We focus on the understanding of the ordering mechanism, a problem that is still not fully comprehended after a decade of research. We combine phenomenological considerations and ab-initio calculations in order to build a simplified model. We use our model to predict the phase diagram of  $\text{IrTe}_2$ . An infinite series of dimerized states is expected as the temperature is lowered, forming a peculiar shape known as Devil's Staircase.

An appendix with the list of acronyms and abbreviations, as well as a complete list of bibliographic references, is given at the end.

# Chapter 1

## Magnetic monopoles, toroidal moments and non-reciprocal magnons in hexagonal Manganites and Ferrites

### 1.1 Introduction

In the study of a material, a great number of factors can affect its characteristics. The possible sources of interesting properties can be related to the contemporary presence of several ingredients, i.e. the particular composition of the material, the oxidation states of the individual atoms, the geometrical disposition of its elements, the presence of order or symmetries, the breaking of symmetries, the presence of lattice distortions, and competing internal forces.

Different behaviors in the materials are observed as one or more of these characteristics become dominant over the others. We distinguish the materials according to these behaviors, classifying them into macro categories or classes.

A fascinating class of materials that we will focus our attention on is the class of *multiferroics*. As the name suggests multiferroic materials host multiple *ferroic* orders, resulting in a material that may have ferromagnetic and ferroelectric order in the same phase, thus exhibiting both magnetic and ferroelectric properties. In fact, multiferroics show, aside from the already mentioned ferroelectricity and ferromagnetism, a plethora of other properties such as electrostriction, magnetostriction, piezoelectricity, and magnetoelectricity [1]. Multiferroic materials are attracting attention due to their versatility and the great number of potential applications [2].

In this Chapter we will study the magnetic properties of hexagonal  $\text{LuFeO}_3$ , a multiferroic material that, at room temperature, possesses a weak ferromagnetic moment [3, 4]. As the magnetic properties come from the Fe atoms ( $\text{Lu}^{3+}$  is non-magnetic), we model the magnetic subsystem as a stack of layers with a triangular lattice that matches the disposition of Fe atoms inside the material (Fig. 1.1). This study can be generalized to the entire group of hexagonal manganites and ferrites  $\text{RMO}_3$  with R being a rare earth element and M a magnetic ion ( $\text{M}=\text{Mn,Fe}$ ). Magnetic ions in these compounds arrange themselves in triangular layers allowing us to broaden the validity of our model to a great number of materials within this group.

The magnetic properties of the system we are considering are a consequence of the

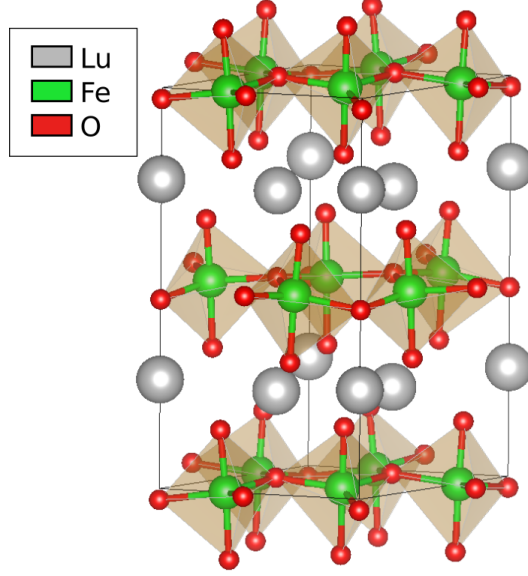


Figure 1.1: Structure of  $\text{LuFeO}_3$  contains the layers of corner-sharing  $\text{FeO}_5$  bipyramids, interspaced with layers of Lu ions (grey), arranged on a triangular lattice. Fe ions with  $S = 5/2$  are positioned in a triangular lattice.

interaction between the magnetic ions of the material. The interaction between nearest neighbor magnetic ions is of the antiferromagnetic (AFM) kind and thus favors an antiparallel orientation of the spins of the ions. The triangular disposition of the ions does not allow for all the spins to be antiparallel on a triangle, due to the odd number of bonds. This situation is referred to as geometric frustration, and forces a different kind of ordering. In this case the frustrated interactions favor an angle of  $120^\circ$  between neighboring spins, as seen in Fig. 1.2.

There are multiple reasons that make AFM triangular lattices worth studying. They host peculiar orders, and the magnetic excitations in the lattice may be utilized to manipulate information without electric currents [5]. Moreover the frustrated spin texture may allow for the presence of particular topological objects e.g. magnetic monopoles, toroidal moments, spirals and skyrmions. Our study will focus on the peculiar magnetic excitations and on two elusive topological objects that can exist in this framework, magnetic monopoles and toroidal moments.

This Chapter has the following structure: we first define the mathematical framework that maps the real material into our model. Semiclassical approximation for spins and Hamiltonian mechanics will be used along with linear spin wave theory to study the dynamics of the spin excitations (magnons). We discuss how the presence of distortions in the real material breaks the symmetry in the lattice and allows for the emergence of magnetic monopoles and toroidal moments. A general analysis of the symmetries of the system is then performed highlighting the most interesting features of the excitations. In the last part a simulation of inelastic neutron scattering shows the magnon spectrum and predicts magnon non-reciprocity within a suitable region of the momentum-space.

## 1.2 Triangular lattice: outline

We model hexagonal  $\text{LuFeO}_3$  with a 2D triangular lattice. This choice is made to mimic the structure of  $\text{LuFeO}_3$  and of hexagonal ferrites and manganites in general.  $\text{Lu}^{3+}$  and  $\text{O}^{2-}$  are nonmagnetic, while  $\text{Fe}^{3+}$  has five unpaired electrons in the outer 3d shell and thus spin equal to  $5/2$ . Fe and Lu atoms are arranged in separate planes with the atoms being the vertices of equilateral triangles, as seen from the structure of the material shown in Fig 1.1. As the magnetic properties only come from Fe atoms we map the real material into a set of 2D planes stacked on top of each other with spins localized at the sites of the lattice and with interlayer and intralayer interactions between spins. It is worth mentioning that the oxygens instead are arranged in six-faced bypyramids with the Fe ions in the center. We will focus more on the role of the oxygens later in this chapter as a small buckling of the bypyramids induces distortions in the material, thus setting the stage for the more intriguing features to be described.

We now discuss the details of the quasi-2D spin lattice model. At this level we only consider spin interactions of the symmetric Heisenberg type: the interaction between two neighboring spins at sites  $i$  and  $j$  will be of the type  $\mathbf{S}_i \cdot \mathbf{S}_j$ . It is known from experiments [6] that in-plane interactions are of the AFM type, so if we only have two spins the interaction energy has the form

$$\mathcal{H}_{int}^{ij} = J \mathbf{S}_i \cdot \mathbf{S}_j \quad (1.1)$$

where  $J > 0$  is the AFM coupling constant and the energy is minimized if the scalar product of the spins is equal to  $-1$  i.e. the spins are antiparallel. In the 2D lattice the situation is less trivial because the triangular arrangement of spins does not allow for a trivial (parallel or antiparallel) configuration of spins. Let us consider the easiest non-trivial case, that of three spins on the vertices of an equilateral triangle (Fig. 1.2).

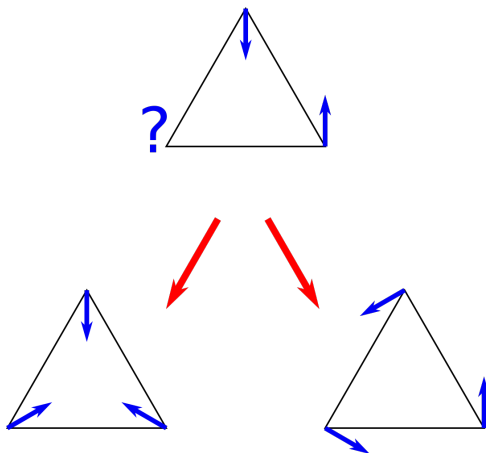


Figure 1.2: Frustration of three spins on the vertices of a triangle. As it is not possible for the three spins to be all antiparallel at the same time a new configuration is favoured and the spins arrange themselves with an angle of  $120^\circ$  between each other.

The Heisenberg interaction of three spins is described by the Hamiltonian

$$\mathcal{H} = J(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_1 \cdot \mathbf{S}_3 + \mathbf{S}_2 \cdot \mathbf{S}_3) \quad (1.2)$$

which can be rewritten as

$$\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_1 \cdot \mathbf{S}_3 + \mathbf{S}_2 \cdot \mathbf{S}_3 = \frac{1}{2}[(\mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3)^2 - (\mathbf{S}_1^2 + \mathbf{S}_2^2 + \mathbf{S}_3^2)] \quad (1.3)$$

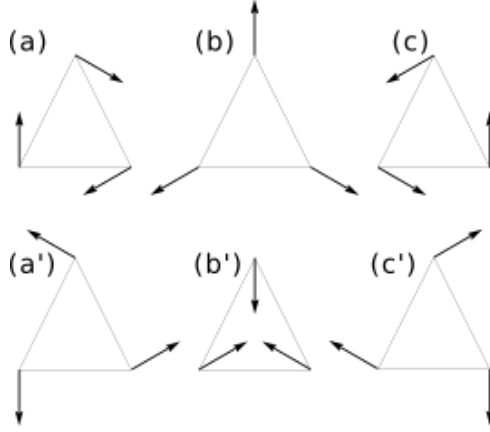


Figure 1.3: Possible spin configurations, compatible with a triangular lattice. (a,c) Inward and (a',c') outward toroidal moment. (b) Outward and (b') inward monopole. A monopole is generated on a triangle between two opposite toroidal moments. Notice that outward toroidal moments are associated to inward monopole and vice versa.

thus, redefining the energy up to a constant. We can then rewrite Eq. (1.2) as

$$\mathcal{H} = \frac{J}{2}(\mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3)^2 \quad (1.4)$$

which is minimized when  $\mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3 = 0$ . As all spins have the same modulus, this condition is realized when the angle between two spins is  $120^\circ$ .

Extending this argument to an infinite 2D lattice, we see that the directions of all spins on the lattice are completely defined once one single triangle on the lattice is fixed, the triangles composing the lattice adopt two (four if we consider an inward or outward orientation) possible spin configurations that we will call monopolar and toroidal configurations (Fig. 1.3). We refer to these textures as “magnetic monopoles” and “toroidal moments” in reference to the hypothetical particles that would create the associated magnetic field lines [7]. In the monopolar case the magnetic field lines are directed towards the center of the triangle, inward or outward, like it would be if a single hypothetical magnetic charge was positioned there. In a similar way the magnetic field in the toroidal configuration runs around the triangle in a torus-shaped way or, equivalently, like if a current perpendicular to the triangle plane was running through the center of the triangle. We can clarify these definitions by associating to the monopolar configuration a “monopolar charge” or “monopolar magnitude”  $\mathbf{r}_i \cdot \mathbf{S}_i$  and by defining properly the toroidal moment as  $\mathbf{r}_i \times \mathbf{S}_i$  where a summation over the index  $i = 1, 2, 3$  is considered. These quantities are respectively maximized for pure monopolar and toroidal configurations.

However, there is one last consideration that we must make: in a perfect 2D triangular lattice all triangles have the same size, are equivalent, and thus when an infinite lattice exhibits the alternating monopolar and toroidal order the different contributions of the two objects cancel each other. To better understand this last statement we must point out that the alternating monopoles and toroidal moments on the lattice can be thought of in terms of opposite toroidal moments. A monopole can in fact be thought as the transition region between two opposite toroidal moments (Fig. 1.3 (b,b')). With this configuration in mind it is easier to comprehend that for equivalent triangles magnetic monopoles and toroidal moments (or equivalently opposite toroidal moments) will compensate each other to a net zero contribution and no macroscopic order.

As we anticipated in the introduction there is a key factor that provides for the existence of monopolar or toroidal order that breaks the duality we describe above. It allows for one of the two configurations to become dominant in the total balance and to establish an ordering for the whole material. We refer to distortions in the material that induce trimerization of the triangles [8]. (Fig. 1.4).

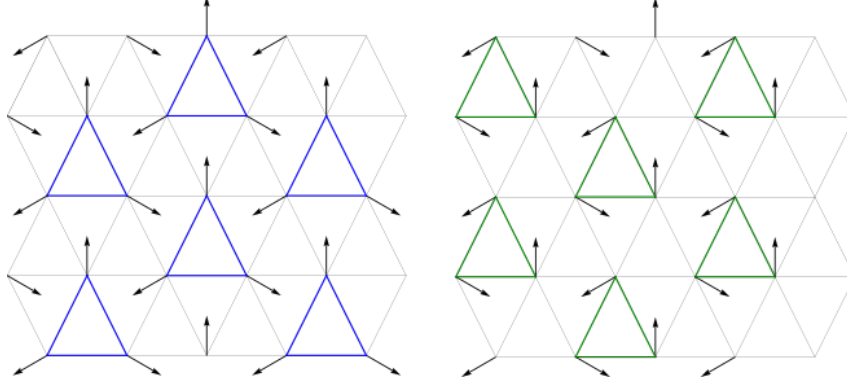


Figure 1.4: Trimerization in the lattice: as some bonds become shorter the strength of the bonding increases thus making some triangles inequivalent to the others. The contribution from the monopole charge (blue) or from the toroidal moment (green) of these triangles (bold in figure) will be greater than the regular ones, hence defining a global monopolar or toroidal order for the whole material.

This argument is general for hexagonal manganites and ferrites. As oxygen atoms are positioned around one central iron atom to form triangular bipyramids (Fig. 1.1) it is possible for the axes of these pyramids to cant. Corner-sharing bipyramids are interconnected among each other, therefore the tilting of a single bipyramid affects the others too. We observe that a buckling of three bipyramids towards the center of the iron triangle makes that triangle smaller (i.e. the bonds between irons are stronger), but at the same time this causes the nearby triangles to become bigger (i.e. with weaker bonds) because of the shared apical oxygen moving away from the center of the triangle (Fig. 1.5).

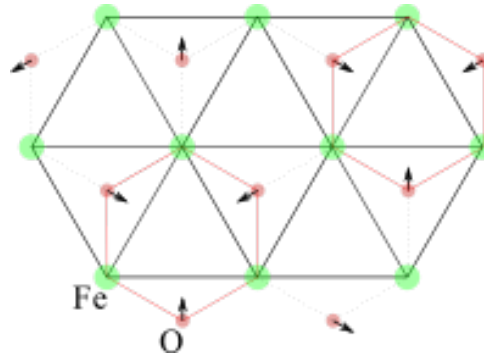


Figure 1.5: Trimerization due to buckling of bipyramids. Oxygens (red) are responsible for the exchange interaction between iron ions (green). As the oxygen bipyramids are tilted, apical oxygens move towards the center of an iron triangle (red hexagons), therefore strengthening the bonds and making the bonds of nearby triangles weaker.

### 1.3 Hamiltonian of the system

In this section we describe the model developed to study the magnetic excitations in the 2D lattice introduced in the previous section, and our method to solve it. The Hamiltonian we use is the following

$$\mathcal{H} = \sum_{ij} (J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{D}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j) + \sum_i (-K(\mathbf{S}_i \cdot \mathbf{n}_i)^2 + K'(S_i^z)^2 - g\mu_B \mathbf{H} \cdot \mathbf{S}_i). \quad (1.5)$$

The first term describes the intralayer AFM Heisenberg interaction and the FM interlayer interaction as the site indices  $i$  and  $j$  select spins belonging to the same plane or to two adjacent planes. The second term describes the antisymmetric Dzyaloshinskii-Moriya (DM) interaction [9, 10, 11] between nearest neighbor (NN) spins in the same plane [12]. The DM vector  $\mathbf{D}_{ij} = \alpha_{DM} \mathbf{r}_{ij} \times \boldsymbol{\delta}$  is computed from the structural data of the material. Here  $\alpha_{DM}$  is a coupling constant, while  $\mathbf{r}_{ij}$  connects two neighboring irons at sites  $i$  and  $j$ ;  $\boldsymbol{\delta}$  connects the middle point of  $\mathbf{r}_{ij}$  to the closest oxygen. The terms with  $K$  and  $K'$  are anisotropy terms. The term with  $K$  represents the easy axis anisotropy within  $ab$ -plane, induced by trimerization, and  $\mathbf{n}_i$  are the shifts of apical oxygens projected in the  $ab$ -plane.  $K'$  defines a hard-axis anisotropy that is perpendicular to the iron layers and forces the spin to lay in the 2D plane. The last term describes the effects of an external magnetic field  $\mathbf{H}$  on the spins,  $g = -2$  is the gyromagnetic ratio and  $\mu_B$  the Bohr magneton.

We are able to select between a state that favours toroidal order over the monopolar one, or vice versa by manipulating the parameters in the model. In particular it is sufficient to only alter two parameters in the model to obtain the configurations we want to explore: the easy axis constant  $K$  and the interlayer coupling  $J'$ . By changing the sign of  $K$  we rotate the easy axis by  $90^\circ$  which transforms the easy direction into a hard direction.

This affects the spin structure: a positive  $K$  sets the easy direction along the shifts of the apical oxygens, thus leading to monopolar ordering (e.g. A2 and B1 phases in Fig. 1.6), while a negative  $K$  leads to a perpendicular in-plane direction to be an easy one, resulting in toroidal states, such as A1 and B2 in Fig. 1.6). Therefore if, for example, before the switching of anisotropy the spins were arranged in monopolar order, after the rotation of the easy axis we would have a toroidal order as the dominant one. Hence the sign of  $K$  selects one of the two possible states in each layer, monopolar or toroidal.

The sign of  $J'$  instead sets the relative orientation of spins in adjacent magnetic layers, so that for FM  $J'$  ( $J' < 0$ ) the toroidal moments or monopolar charges in adjacent planes are the same, and for  $J' > 0$  they alternate. Therefore the number of possible phases selected by  $K$  and  $J'$  is four. Fig. 1.6 shows the four phases that in literature are denoted as  $A_1$ ,  $A_2$ ,  $B_1$ ,  $B_2$  [13]. For example,  $K < 0$  and  $J' < 0$  results in a toroidal order with the same toroidal moment in all magnetic layers, as seen in the A1 state.

### 1.4 Monopoles, toroidal moments and non-reciprocity

In Section 1.2 we explained that the  $120^\circ$  spin order in conjunction with lattice trimerization may lead to the emergence of a toroidal or monopolar order. Strikingly, these orders result in non-reciprocal magnon propagation, a phenomenon that leads to a different absorption of neutrons with opposite wavevectors. Of fundamental importance for this endeavor will be the non-reciprocal character of particular magnons that we first identify with a general symmetry analysis. In the following section we simulate INS spectra to



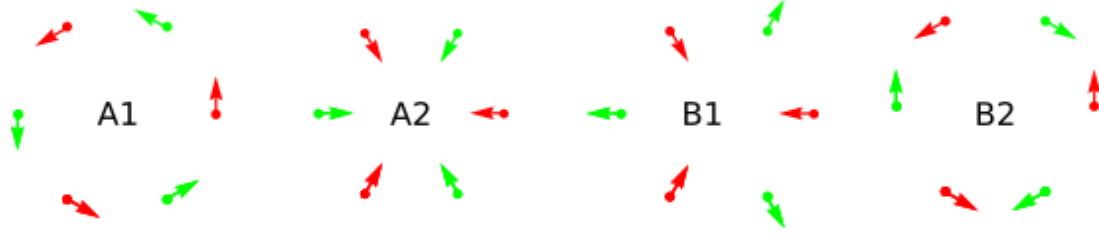


Figure 1.6: The four spin configurations that we considered. Red and green arrows represent spins from two adjacent layers. Configurations A1 (B1) and B2 (A2) are toroidal (monopolar) phases with, respectively, FM and AFM interlayer coupling.

demonstrate how they can be used to identify the monopolar and toroidal states and discriminate between them.

	$2_{001} (00\frac{1}{2})$	$2_{110}$	$I$	$3_z$	$T$
$(\mathbf{r}_i \times \mathbf{S}_i)_z$	+	—	—	+	—
$\mathbf{r}_i \cdot \mathbf{S}_i$	+	+	—	+	—
$k_z$	+	—	—	+	—
$P_z$	+	—	—	+	+
$H_z$	+	—	+	+	—
$(\mathbf{k} \times \mathbf{H})_z$	+	—	—	+	+
Phases					
$A_1$	+	—	—	+	—
$A_2$	+	+	—	+	—
$B_1$	—	+	+	+	—
$B_2$	—	—	+	+	—

Table 1.1: Transformation properties of relevant physical quantities (toroidal moment, monopolar charge; wave vector, ferroelectric polarization and magnetic field components; Pointing vector of the electromagnetic field; order parameters of magnetic phases) under the generators of the group  $P6_3/mmc$ . Notice that phases  $A_1$  and  $A_2$  transform, respectively, as a toroidal moment and a magnetic monopole.  $2_{001}$  is a  $180^\circ$  rotation around  $c$  axis, combined with a translation along  $c$  by half a cell constant;  $2_{110}$  is a  $180^\circ$  rotation around  $[110]$  axis,  $I$  is the inversion operation,  $3_z$  is  $120^\circ$  rotation around  $c$  axis;  $T$  is the time reversal operation.

We now proceed with a systematic symmetry analysis of the different orders we just introduced. This analysis allows us to extract general information that will be used as a guide to drive our study. Table 1.1 shows the transformation properties of important physical quantities under the generators of the group  $P6_3/mmc$ , a high-temperature parent structure of hexagonal ferrites. This information is of fundamental importance as it tells us how to combine different objects to obtain symmetry-allowed terms that may contribute to the symmetry invariants such as a neutron absorption cross-section, magnon dispersion, or a free energy of the system. The presence of wave vector-odd terms in the magnon dispersion signifies non-reciprocal effects. We will show that terms that induce non-reciprocal propagation of magnons are allowed by symmetry. The following statements follow from this analysis:

- A toroidal moment along the  $c$  axis  $(\mathbf{r}_i \times \mathbf{S}_i)_z$  can generate a non-reciprocal magnon in that direction. This is due to the term  $k_z(\mathbf{r}_i \times \mathbf{S}_i)_z$  being invariant under all

the symmetries of  $P6_3/mmc$ . The immediate implications are that INS data should report a contribution to the magnon dispersion  $\omega(\mathbf{k})$  that is linear in  $k_z$ , i.e. non reciprocal, as in fact our simulation does in Fig. 1.7(e);

- On the contrary, the presence of monopoles alone (with  $P_z = 0$ ) cannot induce non-reciprocity of spin wave propagation along the  $c$  axis, because  $k_z(\mathbf{r} \cdot \mathbf{S})$  is not invariant. As there are no contributions to  $\omega(\mathbf{k})$ , linear in the components of  $k$ , there is only reciprocal propagation, as seen in the simulated spectra in Fig. 1.9(f);
- Non reciprocal spin waves are still possible in the presence of monopoles. In fact, an invariant term  $P_z[\mathbf{k} \times \mathbf{H}]_z$  is allowed. When  $\mathbf{k}$  and  $\mathbf{H}$  are in the  $[ab]$  plane, the invariant term is exactly  $\mathbf{P} \cdot [\mathbf{k} \times \mathbf{H}]$  which is equivalent to  $\mathbf{k} \cdot [\mathbf{H} \times \mathbf{P}]$ . If the polarization is parallel to the  $c$  axis, the term  $\mathbf{H} \times \mathbf{P}$  is only in-plane and non-reciprocal magnon propagation in the  $ab$  plane is possible.
- Magneto-electric (ME) effect results from the presence of monopoles. The term  $(\vec{r} \cdot \vec{S})P_z H_z$  is an invariant quantity and it introduces a coupling between an external magnetic field and the polarization inside the material.

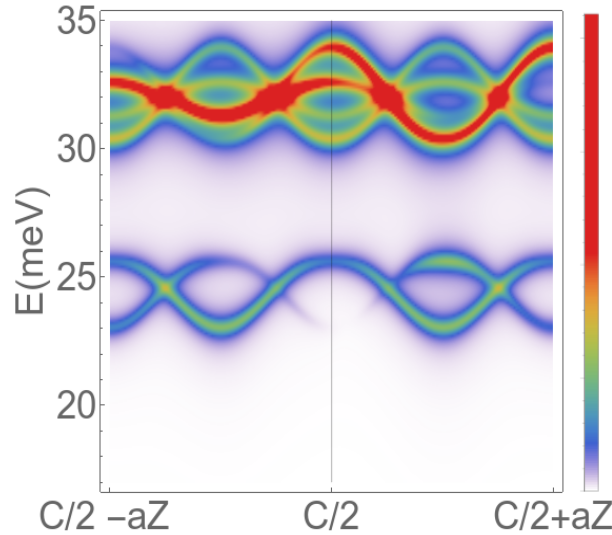


Figure 1.7: Non reciprocal magnon in INS simulation, computed in a toroidal phase.  $C/2$  is the middle point between  $C$  and  $\Gamma$  points (cf. Fig. 1.8(c)), “ $aZ$ ” refers to a small deviation from  $C/2$  along  $k_z$  direction. Further details on this figure, and discussion of the methods used to compute the INS data are provided in Section 1.6.

An important clarification must be made: our symmetry analysis describes terms that are allowed by symmetry in the magnon dispersion, but it gives no information on the constants that come with them. We cannot yet establish which terms give important contributions and which are negligible. As such, in the following INS simulations we were able to see magnon non-reciprocity along  $k_z$  in the toroidal state, while the in-plane non-reciprocity in the monopolar state is not seen.

## 1.5 Magnetic dynamics

We now focus on computing the spin dynamics generated by the Hamiltonian (1.5). In order to obtain magnon excitations and a correct description of inelastic neutron scattering we use linear spin wave theory. For  $S = 5/2$  a semiclassical treatment is justified. Because the modulus of spins is constant, we can express a generic spin at site  $i$  in terms of spherical coordinates with angles  $(\theta_i, \phi_i)$

$$\mathbf{S}_i = (\sin \theta_i \cos \phi_i, \sin \theta_i \sin \phi_i, \cos \theta_i) \quad (1.6)$$

We expand the Hamiltonian around its ground state, characterized by  $\theta_{i0}, \phi_{i0}$ , the values at the minimum of the spherical coordinates  $\theta$  and  $\phi$  of the spin at site  $i$ . Then we introduce  $\alpha_i$  and  $\beta_i$  as small deviations from the ground state so the rule for the expansion will have the form

$$\begin{aligned} \theta_i &= \theta_{i0} + \alpha_i, \\ \phi_i &= \phi_{i0} + \beta_i. \end{aligned} \quad (1.7)$$

With this choice of coordinates the Hamilton equations are:

$$\begin{aligned} \dot{\theta}_i \sin \theta_i &= \frac{\partial \mathcal{H}}{\partial \phi_i} \\ \dot{\phi}_i \sin \theta_i &= -\frac{\partial \mathcal{H}}{\partial \theta_i}. \end{aligned} \quad (1.8)$$

It is straightforward to justify the  $\sin \theta$  term and the shape of these equations if we consider the equivalent Lagrangian formulation [14].

$$\mathcal{L} = \sum_i \dot{\phi}_i \cos \theta_i - \mathcal{H}. \quad (1.9)$$

After expanding the Hamiltonian around the ground state, equations (1.8) take the form:

$$\begin{aligned} \dot{\alpha}_i &= \frac{1}{\sin \theta_{i0}} \frac{\partial \mathcal{H}}{\partial \beta_i}, \\ \dot{\beta}_i &= -\frac{1}{\sin \theta_{i0}} \frac{\partial \mathcal{H}}{\partial \alpha_i}. \end{aligned} \quad (1.10)$$

The ground state around which we expand the equations is computed through a numeric minimization of Eq. (1.5). The resulting configuration is very close to the  $120^\circ$  spin order we described in the previous section, with small deviations due to the DM term and the easy axis anisotropy term that, being driven by the oxygen displacements, slightly moves the spins away from the ideal  $120^\circ$  order. This expansion makes possible an analytical solution of the equation of motion and allow prediction of the magnon spectrum. More details are given in Appendix B. In order to gain insight into the spectrum, we need to move the problem into the Fourier space. To do so, we use the transformations,

$$\beta_j = e^{i\mathbf{k}\mathbf{r}_j - i\omega t} \beta_k, \quad \alpha_j = e^{i\mathbf{k}\mathbf{r}_j - i\omega t} \alpha_k \quad (1.11)$$

where  $\mathbf{k}$  is the momentum vector,  $\mathbf{r}$  is the lattice vector and  $\omega$  is the frequency. Thus in the Fourier space the equation of motions take the form of an eigenvalue problem:

$$(A - i\omega \mathbb{1}) \begin{pmatrix} \alpha_k \\ \beta_k \end{pmatrix} = 0, \quad A = \begin{pmatrix} \partial_{\beta_i} \alpha_j & \partial_{\beta_i} \beta_j \\ -\partial_{\alpha_i} \alpha_j & -\partial_{\alpha_i} \beta_j \end{pmatrix} \mathcal{H}. \quad (1.12)$$

Here  $A$  is the  $2n \times 2n$  matrix of the second derivatives of the Hamiltonian with respect to  $\alpha_k$ ,  $\beta_k$ , and  $n$  is the number of spins in the unit cell. We can now obtain the entire spectrum of the system by solving the eigenvalue problem, Eq. (1.12), thus obtaining the frequency (energy) of the magnons as a function of the momentum  $\mathbf{k}$ . In the next section we will show how to compute the response of the system to an external beam of neutrons.

## 1.6 Unpolarized inelastic neutron scattering

In the previous section we have built a general Hamiltonian of the system under study, expanded it around its ground state and showed how to obtain the magnon frequencies from the Hamilton equations. We now utilize this procedure to simulate INS spectra in the case of monopolar and toroidal orders, so that we can compare the results from our model with experimental data.

Neutrons are a powerful probe to investigate the inner magnetic structure of a material. As they possess no electric charge, they can travel through matter without being disturbed by atomic electric fields. They possess a magnetic moment  $\mu_N$  that is responsible for the magnetic interaction with the spins in the material. Due to the small size of the nucleus compared to the neutron de-Broglie wavelength, the atomic part of the interaction is described by a delta-function, leading to an isotropic atomic scattering cross-section. Therefore neutrons proved themselves to be a useful and relatively clean probe to measure the magnetic excitations and lattice vibrations of materials. We represent the neutron beam by an oscillating magnetic field  $\vec{h}e^{-i\Omega t}$ , where the frequency  $\Omega$  is related to the energy of the beam. When a neutron of frequency  $\Omega$  interacts with the material it can excite a magnon with the same frequency (if a mode with that frequency is present). When this happens the momentum of the neutron changes. When it is collected by the detector, the comparative difference with the initial momentum gives information on the magnons that have been excited by the neutron. In this way, it is possible to compute the spectral function for the magnons by computing the cross section of the interaction between neutrons and the system. The action of the neutron beam will act as an external force term in Eq. (1.12). We can now reformulate the problem including the external contributions

$$(A - i\omega\mathbb{1}) \begin{pmatrix} \alpha_k \\ \beta_k \end{pmatrix} e^{-i\omega t} = \begin{pmatrix} h_\alpha \\ h_\beta \end{pmatrix} e^{-i\Omega t}, \quad (1.13)$$

with  $h_\alpha$  and  $h_\beta$  being the terms in  $\vec{S} \cdot \vec{h}$ , linear in  $\alpha_i$  and  $\beta_i$ , respectively.

We keep the time-dependent exponential terms with  $\omega$  and  $\Omega$  to explain in detail the following point: the system will respond to the oscillating magnetic field only if the field associated with the neutrons has the same frequency as one of the magnons in the spectrum. Mathematically this is apparent from the Fourier transform of the system, where the two time-dependent exponential terms give rise to  $e^{-i(\omega-\Omega)t}$ , that is a highly oscillating integrand for different frequencies. Non-zero contributions result only when  $\omega = \Omega$ , meaning that the neutron beam excites a magnon only if it has the frequency (energy) matching one of the magnons.

Solving Eq. (1.13) for all  $\omega$  gives expressions for  $\alpha_k$  and  $\beta_k$  as functions of  $\omega$ ; if we substitute  $\alpha_k$  and  $\beta_k$  in the spherical coordinate expression for  $\mathbf{S}$ , we can express the spin response to the external magnetic field as an  $\omega$  and  $k$  dependent quantity. To obtain the magnetic cross section we need to compute the magnetic susceptibility tensor, which, for

the uniform spiral in the  $xy$  plane takes the form:

$$\chi_{ij}(\omega, k) = \frac{g\mu_B}{V} \frac{\partial S^{(i)}(\omega, k)}{\partial h^{(j)}(\omega, -k)}, \quad (1.14)$$

where  $V$  is the volume of the unit cell.

In the experiment [15] a non-polarized neutron beam is used, therefore we must average over all possible spin polarizations of the neutrons. The expression for the INS cross section due to magnetic dipole-dipole interactions of spins with neutrons in a non-polarized neutron beam is given by [16]

$$\frac{d^2\sigma}{dEd\Omega} \sim \sum_{ij} \left( \delta_{ij} - \frac{k_i k_j}{k^2} \right) \chi_{ij}. \quad (1.15)$$

Equation (1.15) can be easily generalized to the polarized neutron scattering case by introducing operators that project onto one of the spin polarizations.

We have defined the theoretical framework to simulate an INS experiment. The only undefined quantities are now the parameters that appear in the model (1.5). We use the parameter values of  $J = 2.8$  meV,  $|J'| = 0.3$  meV,  $H_x = 2$  T,  $K' = 0.3$  meV,  $|K| = 0.68$  meV/Å<sup>2</sup>,  $\alpha_{DM} = 0.05$  meV/Å<sup>2</sup>. These values are chosen to reproduce the experimental inelastic neutron scattering data (Fig. 1.8) [15]. The values for  $J$  and  $K$  were chosen according to published values [15], while we adopted the above values of the remaining parameters to better match the simulated spectra with the experimental ones. Particular attention was given to the gap at the  $\Gamma$  point in the spectrum and the energy of the plateaux between  $A$  and  $B$  points. We tuned the parameters of the model to describe these experimental features.

INS spectra for toroidal and monopolar orders A1 and A2 are reported in Fig. 1.9. We see from panels (a-b) that the differences between the two spectra in the plane  $[k_x, k_y]$  are present but small. As we did not observe in-plane non reciprocity, we suppose that even if these non-reciprocal magnons are allowed in monopolar state the actual non-reciprocal contribution to the magnon dispersion is negligible. In panel (e) non-reciprocity along  $k_z$  is evident, consistent with the expectations from our symmetry analysis.

A more extensive study of the different phases is portrayed in Figures 1.10 and 1.11. We plotted the simulated INS spectra for all four orders under the same parameters as used for Fig. 1.9. Additionally, we verified the effect of DM interaction on the spectrum. We show that the observed non-reciprocity in A1 is independent of the presence of DM interaction. The state B2 displays non reciprocal behaviour only for high valued DM, highlighting a weak non-reciprocal character of the magnon.

### 1.6.1 Magnetic quadrupole contribution

In our study so far we did not consider the possible presence of magnetic quadrupole moments. Monopoles and toroidal moments are terms of multipole expansion of the general vector potential  $\mathcal{A}$ . As is common in this kind of expansions, higher order terms give small corrections with respect to lower-order terms. Monopoles and toroidal moments appear in this expansion, respectively, as zero-order and second-order terms [17] (first order terms are magnetic dipoles that are absent in our system). The second order expansion also includes a quadrupole moment. This is why, in principle, the magnetic

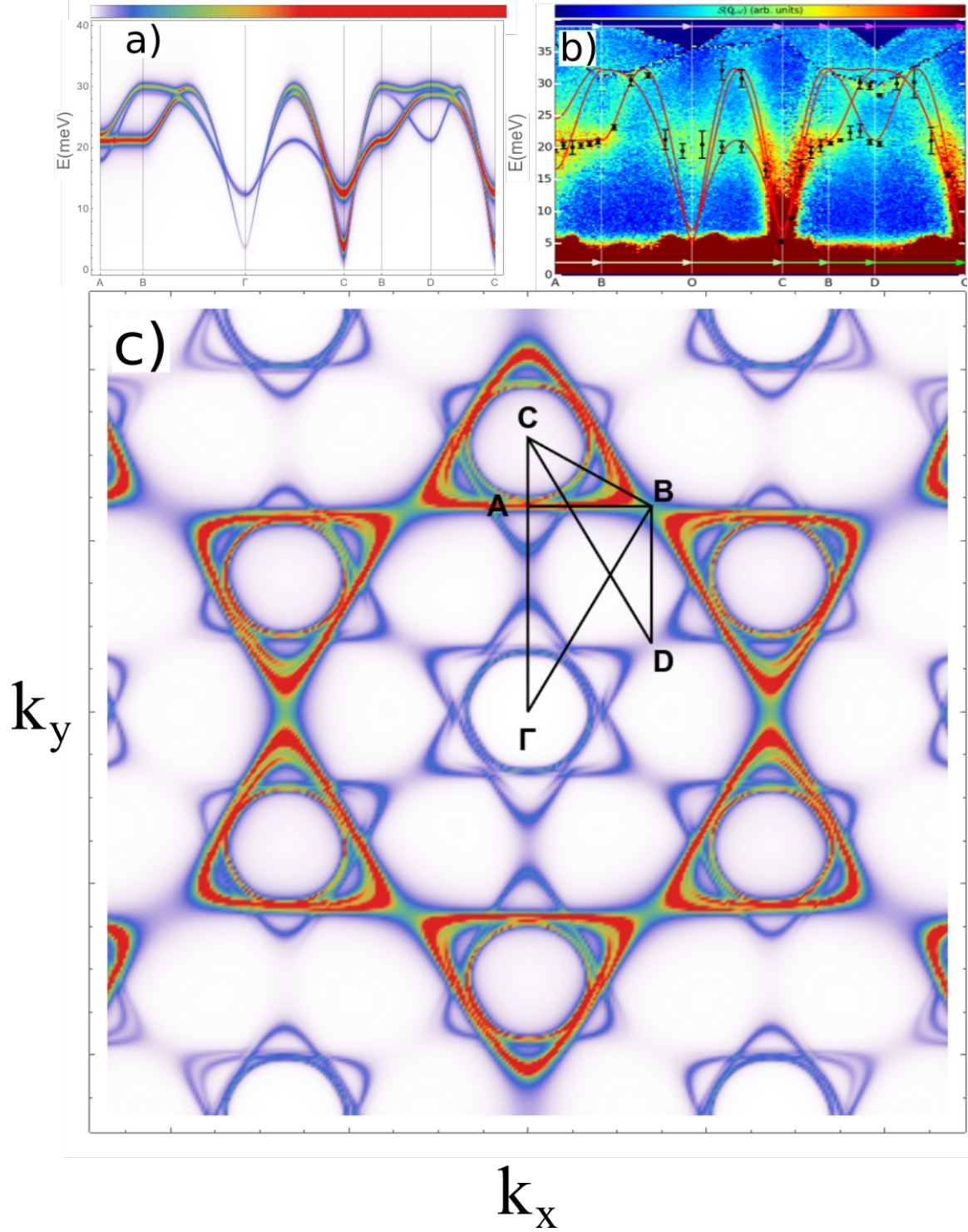


Figure 1.8: INS simulation: (a) simulated neutron scattering cross-section for  $\text{LuFeO}_3$ , color scale encodes INS cross section. The values of the parameters used in the simulation are chosen to match the features of the experimental data from [15] (that are shown in Panel (b)). (c) Constant energy cut  $E = 20$  meV of the simulated neutron scattering cross-section. The path used in (a) and (b) is indicated with black solid lines.



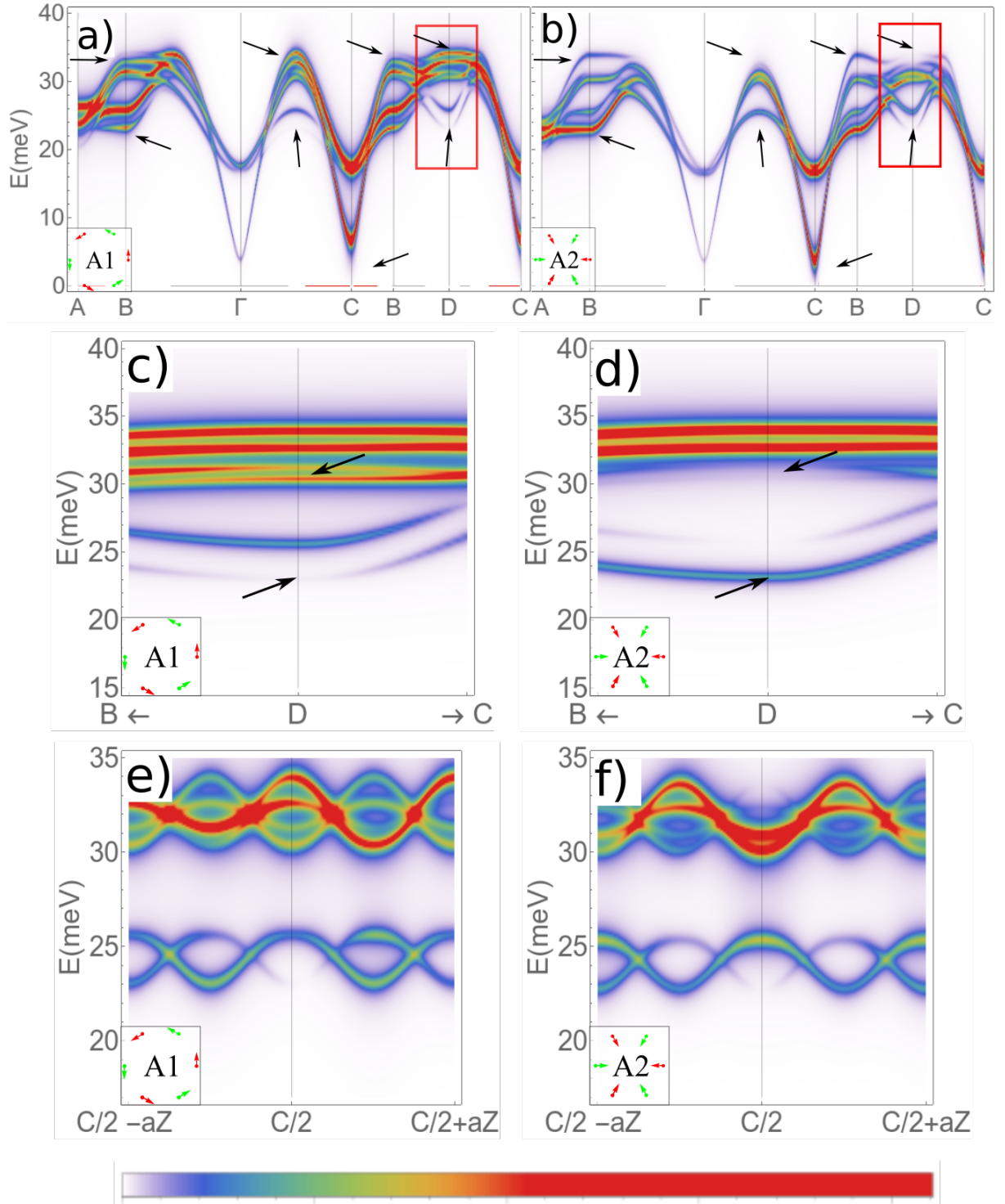


Figure 1.9: INS computed for A1 (toroidal) and A2 (monopolar) phases, shown in insets. Color scale encodes INS cross section. (a-b) inelastic neutron scattering intensity computed along the  $k$ -path defined in Fig. 1.8(c). Arrows point to the differences between the two phases. The red box highlights the region that is enlarged in panels (c-d). (e-f) Close-up on a midpoint of C- $\Gamma$  interval: INS intensity along  $k_z$  direction. “aZ” refers to a small deviation from C/2 along  $k_z$  direction. Non-reciprocal magnon excitation is evident in panel (e), where the excitation intensity is not symmetric.

quadrupole moment could give contributions as important as the toroidal moment. The second-order contributions to the vector potential are

$$\begin{aligned}\langle \mathcal{A}_{quad}^{(2)}(R) \rangle_i &= -\epsilon_{ijk} q_{kl} \partial_j \partial_l \frac{1}{R}, \\ \langle \vec{\mathcal{A}}_{tor}^{(2)}(R) \rangle &= \nabla(\vec{t} \cdot \nabla) \frac{1}{R} + 4\pi \mathbf{t} \delta(\vec{R}),\end{aligned}\tag{1.16}$$

where  $\langle \dots \rangle$  represents the time average and  $q_{kl}$  and  $\mathbf{t}$  are the quadrupolar and toroidal moments:

$$\mathbf{t} = -\frac{1}{2} g \mu_B \sum_{\alpha} \mathbf{r}_{\alpha} \times \mathbf{S}_{\alpha},\tag{1.17}$$

$$q_{ij} = -\frac{g \mu_B}{2} \sum_{\alpha} (S_{\alpha i} r_{\alpha j} + S_{\alpha j} r_{\alpha i}),\tag{1.18}$$

where the index  $\alpha$  runs over the different spins that contribute to  $\mathbf{t}$  or  $q_{ij}$ .

As the symmetry analysis in Table 1.1 shows, in the presence of a toroidal moment a non-reciprocal magnon is generated. We want to verify if the quadrupolar moment contributes to non-reciprocity too, i.e. if there exists an invariant, linear in  $\mathbf{k}$ , that contains  $q$ . We can greatly simplify the expression for  $q$  by taking into account that  $q$  is invariant under  $120^\circ$  rotation around the  $z$  axis

$$\begin{pmatrix} -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} q_{11} & q_{12} & q_{13} \\ q_{21} & q_{22} & q_{23} \\ q_{31} & q_{32} & q_{33} \end{pmatrix} = \begin{pmatrix} q'_{11} & q'_{12} & q'_{13} \\ q'_{21} & q'_{22} & q'_{23} \\ q'_{31} & q'_{32} & q'_{33} \end{pmatrix}.\tag{1.19}$$

By imposing  $q_{ij} = q'_{ij}$  it follows that only the  $q_{33}$  component of the quadrupole moment can be non-zero. If no external fields are present, the tensor  $q_{ij}$  can only be contracted with the vectors  $\mathbf{k}$  and  $\mathbf{P}$  in a term like  $k_i q_{ij} P_j$ . In our case, the vector  $P$  is along the  $c$  axis and, given the form of  $q$  from Eq. (1.19), the only possible term is  $k_z q_{33} P_z$ .

Therefore, in principle, the quadrupole moment can contribute to the non-reciprocity of the magnon. However, calculating the quadrupolar moment using Eq. (1.18), we find it to be much smaller than that of the toroidal moment. This reveals that our analysis is not affected by having neglected the quadrupole term in the expansion.

## 1.7 Conclusions

In this Chapter we discussed a mechanism through which a toroidal or monopolar order emerges in a 2D triangular lattice. The particular order arises from a combination of the  $120^\circ$  spin order (due to the frustrated AFM interaction) and the structural trimerization. These two elements are present in general in hexagonal manganites and ferrites, suggesting a generalization of our model for the entire class of materials.

A realistic microscopic model has been used to simulate INS experiments. Good agreement with experimental data is found and validates the reliability of the model. A general symmetry analysis is provided in order to help identify the cases where elusive magnon non-reciprocity is induced by monopoles and toroidal moments. We hope that the predicted magnon non-reciprocity, associated with the presence of toroidal order, will help identify that order in the future experiments.



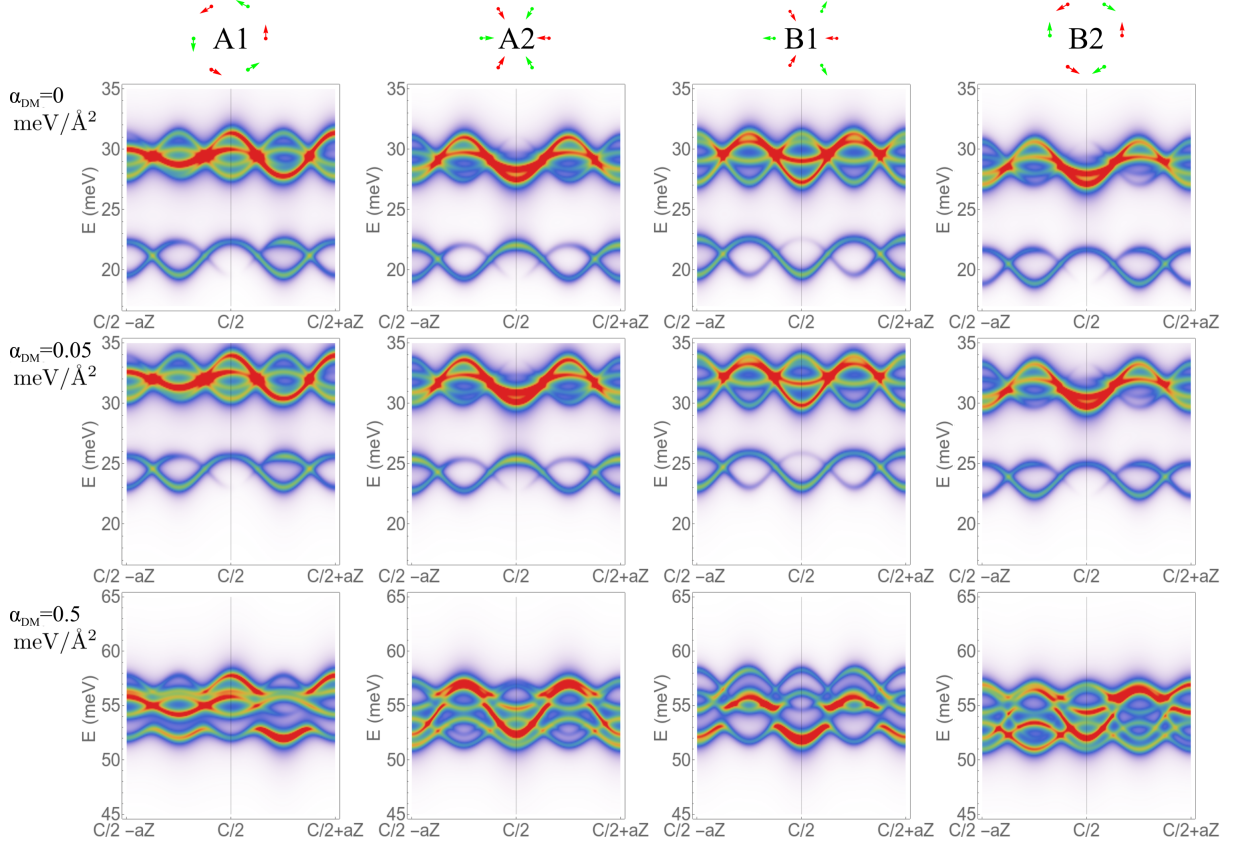


Figure 1.10: INS cross-section plotted near a midpoint of C- $\Gamma$  interval along  $k_z$  for different magnetic phases and for different values of DM interaction. Color scale encodes the INS intensity.

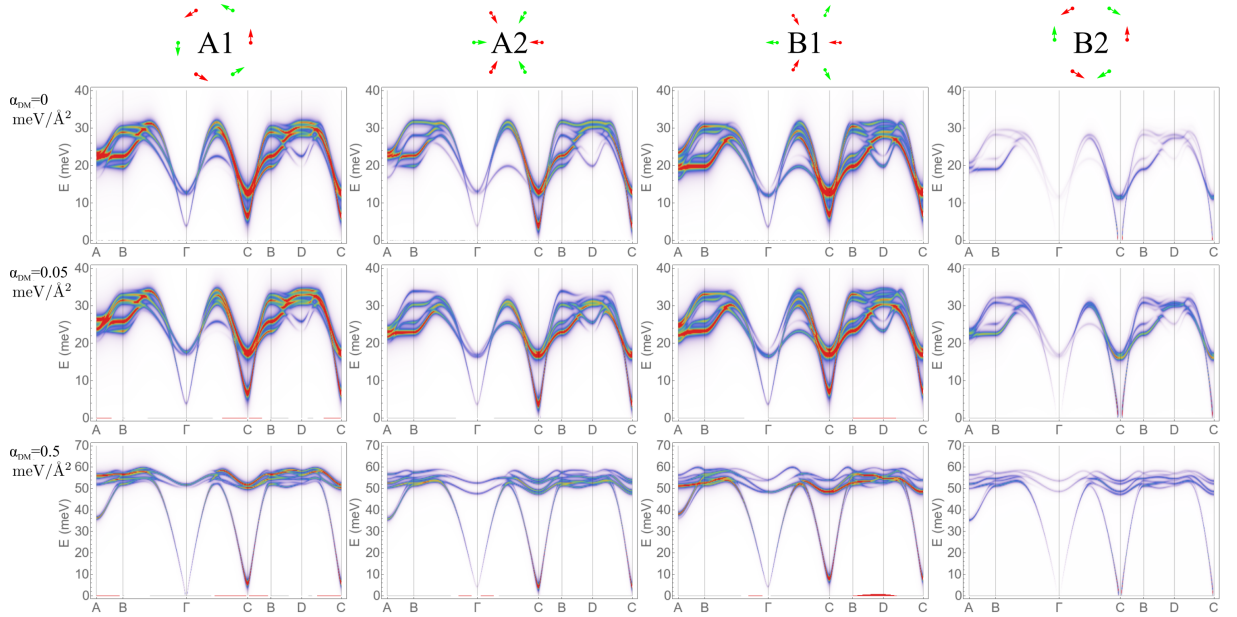


Figure 1.11: Simulated INS spectra along the path shown in Fig. 1.8 for different magnetic phases and different values of DM interaction. “aZ” refers to a small deviation from C/2 along  $k_z$  direction. Color scale encodes the INS intensity.

# Chapter 2

## Study of excitations in spin spiral systems

### 2.1 Introduction

In the previous Chapter we discussed a layered system in which geometrically frustrated magnetic interactions gave rise to monopolar and toroidal orders. In this Chapter we are going to discuss another frustrated system. However, in this case, the frustration is not caused by the geometry but from the competition between nearest and next nearest neighbor exchange interactions, as often encountered in orthorhombic manganites, e.g.  $\text{TbMnO}_3$ . In this case magnetic frustration often results in a configuration where the spins all rotate along the same angle with respect to each other, forming a spin spiral. We focus our attention to the interesting physical properties that arise in a spin spiral, for example the inversion symmetry breaking due to the presence of the spiral induces a ferroelectric polarization [1]. This feature alone opens a wide range of possibilities for multiferroic phenomena. The interaction between magnetic and electric degrees of freedom is a topic of major interest in the field of condensed matter physics as it paves the way for the technological development in controlling magnetic order and magnetic excitations through electric fields [18, 19].

In this Chapter we start with the simplest model for a spiral: a one-dimensional spin chain with competing nearest neighbor (NN) and next nearest neighbor (NNN) interactions. We then discuss the presence of domain walls (DWs) in the spiral. We can describe a DW as the boundary between two regions of the system for which the spirals exhibit different spin rotation sense. DWs are spontaneously formed inside a material during a phase transition.

The spiral configuration, in conjunction with the presence of the DW, sets the proper conditions for the emergence of interesting and non trivial modes inside the material. Among these modes, soft and polar modes are found and they potentially contribute to the dielectric properties of the material. Such modes can affect the system as a whole or can be active only in the single domains or locally on the DW. Our analysis is concentrated on the particular class of chiral DWs. In general we define a system as chiral (from the Greek for *hand*) if it presents two different configurations that are mirror images of each other and are energetically inequivalent. In the case of a spin spiral, a spiral is chiral if one rotation sense of the spins is preferred over the other. A chiral domain is then a region identified by a well defined spin rotation sense; a chiral DW separates two opposite chiral domains. DM interaction, described also in the previous Chapter, favors a rotation sense

for the spin, and thus is a chiral interaction. Furthermore DM interaction relates the rotation sense of the spin to electric polarization, hence chiral DWs are also ferroelectric.

The structure of this Chapter is the following: in the first sections we describe the spiral Ansatz and the compatibility of this configuration with the presence of DWs. We then generalize the case by introducing a quasi 1-D model Hamiltonian. This model includes DM interaction, anisotropy terms and external field terms. With this choice the model may be used to describe real materials that exhibit spiral order, such as  $\text{TbMnO}_3$  and  $\text{MnWO}_4$ . The Hamiltonian is studied for the particular case of a spiral with a single chiral DW. By analysing the excitation spectrum we infer magnetoelectric properties of the spiral magnet [20]. Among the full set of modes we identify a number of low frequency dielectric anomalies that may be the primary cause of hybrid magnon-polar phonon excitations.

The Chapter concludes with a discussion on how the presence of a DW alters the phonon and magnon spectra. A separate section is dedicated to the ME properties of the spiral and the dynamics of the spin texture.

## 2.2 The spiral configuration

The causes for the emergence of a non collinear spin structure inside a material are numerous and quite diverse. It is not possible to write an extensive list for such causes at this level, but significant examples are the following:

- frustrated spin interactions (e.g. DM interactions or competing Heisenberg exchanges);
- geometric constraints bound to the symmetries of the material (as the geometric frustration of the previous Chapter, AFM interaction on triangles);
- non linear effects and high order terms absent in low energy effective theories (4-spins interactions [21, 22]);
- interplay between electric and magnetic degrees of freedom in the material (e.g. DM interaction favors non-collinear states [23]).

In this section the attention is focused on a rather simple spin configuration, a quasi-1D spin spiral. We study this case in order to better understand the generalized model that we will introduce in the next section and that can be use to study real material that exhibit the spiral order ( $\text{TbMnO}_3$ ,  $\text{YMn}_2\text{O}_5$ ,  $\text{MnWO}_4$ ,  $\text{CuO}$  [24, 25, 26, 13])

We now describe how a spiral arises as a ground state of a simple interacting spin Hamiltonian where magnetic frustration is present in the form of competing NN and NNN interactions. The Hamiltonian is

$$H = \sum_i J_1 \mathbf{S}_i \cdot \mathbf{S}_{i+1} + J_2 \mathbf{S}_i \cdot \mathbf{S}_{i+2}, \quad (2.1)$$

here we consider  $J_1 < 0$  and  $J_2 > 0$  as respectively the NN and NNN Heisenber exchange constants, while  $\mathbf{S}_i$  describes the spin at site  $i$  of the chain. We will refer to this Hamiltonian as the  $J_1$ - $J_2$  model. We are looking for a solution that describes a spiral in a plane, therefore we consider the vectors  $\mathbf{S}$  as 2D vectors of unitary length. In polar coordinates

$$\mathbf{S}_i = \{\cos \phi_i, \sin \phi_i\}, \quad (2.2)$$

with this choice of coordinates the scalar product is

$$\mathbf{S}_i \cdot \mathbf{S}_j = \cos(\phi_i - \phi_j). \quad (2.3)$$

We can obtain a spiral solution with the following ansatz: we assume that the spin angle follows the relation  $\phi_n = n\phi_0$ , where we determine the value of  $\phi_0$  through minimization. This choice is also motivated by the translational invariance of the Hamiltonian, we then expect all the spins to rotate the same amount. It follows that Eq. (2.1) becomes

$$H = N(J_1 \cos \phi_0 + J_2 \cos 2\phi_0) \quad (2.4)$$

where  $N$  is the number of spins in the chain. By minimizing the energy with respect to  $\phi_0$  we obtain

$$-J_1 + \sin \phi_0 - 2J_2 \sin 2\phi_0 = 0, \quad (2.5)$$

and, simplifying for  $\sin 2x = 2 \sin x \cos x$ , we have

$$\cos \phi_0 = -\frac{J_1}{4J_2}, \quad (2.6)$$

which gives the expression for the angle  $\phi_0$  in terms of the parameters of the model

$$\phi_0 = \arccos\left(-\frac{J_1}{4J_2}\right). \quad (2.7)$$

This expression gives the value of the fundamental angle of the spiral, but also sets the condition for the spiral solution to appear. For the spiral to exist, the condition  $|J_1/4J_2| < 1$  must be verified. This condition imposes constraints on  $J_1$  and  $J_2$  for the spiral to appear, otherwise the system would stabilize in a FM or AFM pattern. We obtained the angle for the spiral solution, but the rotation verse of the spins is not fixed, the spins can rotate either of  $\phi$  or  $-\phi$ . This happens because the  $J_1$ - $J_2$  does not define a preferred chirality. If, for example, we introduce a DM term, a preferred rotation sense of the spins will be selected.

Another important detail is that  $J_1$  and  $J_2$  depend on the material and, in general, Eq. (2.7) does not result in a rational fraction of  $\pi$ . Therefore the spins will never complete a full rotation in correspondence of a site, i.e. there is no integer number  $n$  such that  $n\phi_0 = 2\pi$ . We define this scenario as *incommensurate* magnetic order.

### 2.2.1 Chiral Domain and Domain Walls

In the previous section we obtained the spiral as a solution of  $J_1$ - $J_2$ . We expect for a material with frustrated magnetic interactions to have a spin spiral configuration as a ground state, but the situation in real materials is more complex.

We refer to spiral order we just described as the “perfect spiral”. In real materials that exhibit spiral order, the spin configuration may differ significantly from the perfect spiral.

The first trivial deviation from the perfect spiral is due to the higher dimensionality of real systems. In a 3D material spins can rotate along the three major directions defined by the lattice vectors. This is not a problem for our case because we are considering materials that shows a modulated magnetic order along only one of the lattice directions (e.g.  $\text{TbMnO}_3$ ) and for which a quasi-1D model can be used. We call our model a “quasi-1D” model because we are considering a 1D chain where the spins can move in a plane.

In the spiral state, the spins rotate along the direction of the wave vector  $\mathbf{q}$  of the spiral, and they do not rotate along the directions perpendicular to  $\mathbf{q}$ . Therefore, we can select  $\mathbf{q}$  as the direction of our  $x$  axis, and describe the spiral state with only one coordinate. For example, let us consider a slightly more complex case: a 2D square lattice with competing  $J_1$ - $J_2$  interactions along the two axes. The periodicity of the system allows for a Fourier analysis, and so we can express the Hamiltonian in Fourier space as

$$H_{\mathbf{q}} = J_1(\cos q_x + \cos q_y) + J_2(\cos 2q_x + \cos 2q_y), \quad (2.8)$$

which is minimized for a certain direction of the vector  $\mathbf{q} = q_x, q_y$ , with  $q_x = q_y$ . We define a coordinate system such that  $\mathbf{x} \parallel \mathbf{q}$ . In this way a 2D spiral configuration is described with a quasi-1D model. Another reason for the system to not have a perfect spiral order is the presence of impurities and defects. In the vicinity of an impurity or a defect, the effective interactions between the spins may be different, thus altering the local spin order in that region.

Finally, the temperature also plays a fundamental role. If a material displays spiral order at low temperature, the system needs to be cooled down to reach the spiral state. The cooling rate across the transition controls the number of chiral domains: a rapid quenching of the temperature leads to higher DW density while a slower cooling allows the coalescence of chiral domains and the DWs to be removed.

Due to these effects is not uncommon for the ground state of a real material to be driven away from the perfect spiral we described. On the contrary, a more “fragmented” spiral order is reached. Fig. 2.1 shows two different spin configurations: the regular spiral (a) with the angle  $\phi_0$  that we obtained in Eq. (2.7) and a “fragmented” spiral (b). In the first all the spins rotate in the same sense around the spiral axis (perpendicular to the plane of the page) while in the latter the spiral changes rotation sense multiple times.

We mentioned in the introduction of this Chapter the concept of *chirality*, Fig. 2.1 provides an example of a perfect spiral (a) and a spiral with chiral domains (b). Two domains of opposite chirality are regions of the spiral where the spin rotate of the same angle but in the opposite sense. Fig. 2.1 (b) shows the rotation angle of the spiral to be either  $\phi_0$  or  $-\phi_0$ . The region of separations between two chiral domains is a chiral DW. We see from our Hamiltonian 2.4, that both angles  $\phi_0$  and  $-\phi_0$  are minima of the same energy, thus in a material without preferred chirality the two rotation senses are equivalent.

In the beginning of this section we stated that the perfect spiral is altered in real materials. A more realistic configuration is, in fact, a multi-domain spiral. We can justify this configuration over the perfect spiral with the following argument: we consider a material that possesses two possible phases, a spiral phase and a non-spiral phase. We do not explore the details of the phase transition but we suppose that it can be properly described in terms of a certain control parameter  $A$ . The phase transition happens at a certain value  $A_0$  of the parameter. The material is in the non spiral phase and  $A \neq A_0$ , as  $A$  gets close to the value  $A_0$  small ordered spiral domains start to appear in random places in the material. As  $A$  approaches  $A_0$  these domains grow, nucleating into bigger domains. We showed that the possible spiral angles  $\phi_0$  and  $-\phi_0$  are energetically equivalent so in different domains the value of this angle is randomly chosen between the two possibilities. When two domains that have different spiral angles merge the boundary region that connects the two forms a DW. As the phase transition happens the material enters the spiral phase and all domains merge. where the spiral angles are different DWs appear inside the material.

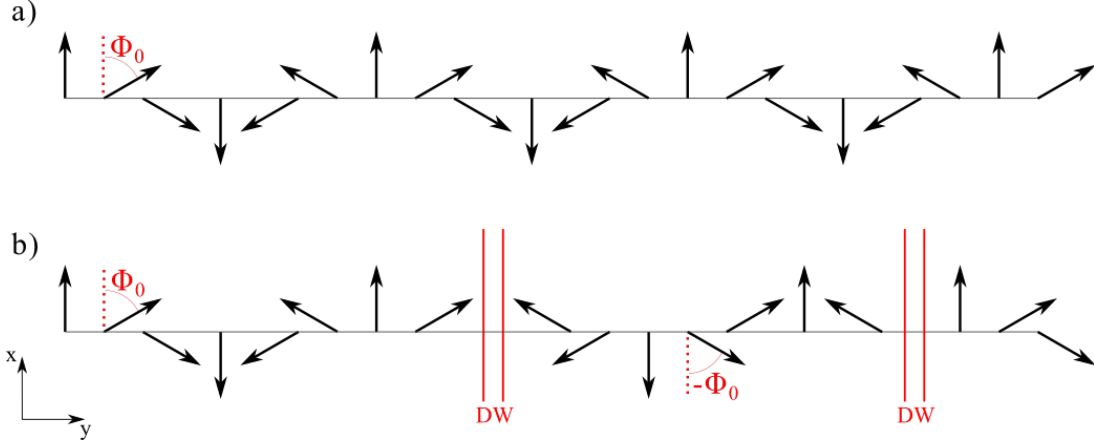


Figure 2.1: (a) “perfect spiral” solution. All spins rotate around the spiral axis ( $\hat{z}$  perpendicular to the page) with the same angle  $\phi_0$ . (b) multiple chiral domains and DWs. Different regions with spin angles  $\phi_0$  and  $-\phi_0$  are present and are connected through their boundaries with chiral DWs.

In the next section we introduce the model suited to study a spiral configuration in presence of a DW, and we use it to analyze the multi-domain configuration that we discussed.

## 2.3 The model

In section 2.2 we showed how a simple  $J_1$ - $J_2$  model results in a spiral arrangement of spins and later we discussed how DWs arise in the spiral. In this section we build a more realistic microscopic model. We generalize a  $J_1$ - $J_2$  model by introducing additional terms describing polar displacements of oxygen ions (e.g. in  $\text{TbMnO}_3$ ) that change the angle of Mn-O-Mn bonds. Therefore, we write the Hamiltonian

$$\begin{aligned}
 H = \sum_i J_1 \mathbf{S}_i \cdot \mathbf{S}_{i+1} + J_2 \mathbf{S}_i \cdot \mathbf{S}_{i+2} + K_h (S_i^z)^2 + \alpha_{\text{DM}} (\mathbf{r}_{12} \times \delta \mathbf{r}_i) \cdot (\mathbf{S}_i \times \mathbf{S}_{i+1}) \\
 + \frac{1}{2m} \boldsymbol{\pi}_i^2 - V_{uc} \mathbf{P}_i \cdot \mathbf{E} + \frac{m\bar{\omega}^2}{2} \delta \mathbf{r}_i^2 + \frac{\gamma}{2} (\delta \mathbf{r}_{i+1} - \delta \mathbf{r}_i)^2,
 \end{aligned}
 \tag{2.9}$$

where  $\mathbf{S}_i$  is the classical spin ( $|\mathbf{S}| = 1$ ) at site  $i$ , and  $J_1$  and  $J_2$  represent competing Heisenberg interactions, as described in Section 2.2.  $K_h$  is the strength of a hard  $c$ -axis anisotropy that forces the spins into the  $ab$  plane as observed e.g. for  $\text{TbMnO}_3$  [24]. The term with  $\alpha_{\text{DM}}$  describes the DM interaction and is responsible for the coupling between spins and electric dipoles.  $\mathbf{P}_i = Z\delta \mathbf{r}_i$  is the polarization due to the polar mode (electric dipole per unit cell volume  $V_{uc}$ ), directly related to the shift  $\delta \mathbf{r}_i$  of oxygen and Mn ions in the unit cell  $i$ .  $Z$  is the mode effective charge. When in the following we refer to oxygen shifts we will consider  $\text{TbMnO}_3$  as a reference.

The DM term is responsible for an effective force on the polar mode  $\delta \mathbf{r}_i$

$$\mathbf{F}_i^{\text{DM}} = -\partial H / \partial \delta \mathbf{r}_i \sim [\mathbf{S}_i \times \mathbf{S}_{i+1}].
 \tag{2.10}$$

This force results in a finite shift  $\delta \mathbf{r}_i$ , and generates a ferroelectric polarization. In particular, the sign of the polarization is determined by the product  $[\mathbf{S}_i \times \mathbf{S}_{i+1}]$ , which is

positive or negative depending on the spin rotation sense, i.e. the chirality of the spiral. Therefore chiral DWs are ferroelectric.  $\mathbf{E}$  is the external electric field. The term with  $\boldsymbol{\pi}_i$  is the kinetic energy associated with the momentum of oxygen ions,  $\boldsymbol{\pi}_i = \{\pi_i^x, \pi_i^y, \pi_i^z\}$  and  $\delta\mathbf{r}_i = \{\delta x_i, \delta y_i, \delta z_i\}$  are in fact canonical variables and  $\bar{\omega}$  is the frequency of the polar optical mode [27],  $\gamma$  is the stiffness of the polar mode. Finally,  $m$  is the mode effective mass divided by the square of the mode effective charge  $Z$ .

Although more complex than the simple  $J_1$ - $J_2$  model, the solution for this Hamiltonian is still a spiral, as described in more detail in the next Section. However, we will first explain the physics behind the extra terms. The term with  $K_h$  is the hard  $c$ -axis anisotropy. As we are considering  $\text{TbMnO}_3$  as an example, in order to capture its ground state we need the spiral to be confined in the  $ab$  plane of the crystal. This is achieved with the anisotropy term, introducing an energy penalty on the  $z$  components of spins. This forces the ground state spiral to be contained in the  $ab$  plane.

The DM term is introduced to describe the ME effect in the system. Other common sources of ME effect, such as Heisenberg exchange striction, are not considered here. The spin texture is coupled to oxygen shifts  $\delta\mathbf{r}_i$ . In fact, as the magnetic ions interact and the spin arrange themselves into the spiral pattern, polar distortions are induced in the lattice [27, 28, 29]. By coupling the magnetic (spins) and electric (oxygen shifts) degrees of freedom, the DM term introduces the ME effect into the model.

The harmonic oscillator term defines the oscillation frequency of the polar modes at  $\bar{\omega}$ , confining the oscillations of  $\delta\mathbf{r}_i$  into a parabolic potential. The stiffness term, described by the parameter  $\gamma$ , introduces an energy penalty for spatial changes of polarization. It also couples oscillations at different unit cells that would otherwise be only weakly affected by each other through the DM term.

## 2.4 Solution and properties

In Section 2.2 we were able to find analytically a ground state of the Hamiltonian, Eq. (2.1), by imposing a simple spiral ansatz. However the general model that we introduced in the previous section with Eq. (2.9) is more complex and spins are not constrained to the plane

$$\mathbf{S}_i = \{\sin \theta_i \cos \phi_i, \sin \theta_i \sin \phi_i, \cos \theta_i\}. \quad (2.11)$$

It is less straightforward to analytically minimize Eq. (2.9). We are particularly interested in the local minima with DWs. In this regard we minimize the Hamiltonian (2.9) by numerical methods, and find a possible ground state for the system. Periodic boundary conditions are set on a chain of 50 spins and, in this phase, no external electric field is used. The values of the parameters used in the calculations are  $J_1 = 0.3$  meV,  $J_2 = 0.1$  meV,  $V_{uc} = 230$  Å<sup>2</sup> (similar to those in  $\text{TbMnO}_3$  [25, 24]),  $\bar{\omega} = 21$  meV = 5 THz [30],  $K_h = 0.1$  meV,  $m \approx 3m_O/V_{uc}$  with  $m_O$  being the mass of oxygen,  $\alpha_{\text{DM}} = 1$  meV/Å<sup>2</sup>,  $c = 0.3$  meV/Å<sup>2</sup>.

As we explained before, a physical system will likely have different chiral domains connected by DWs. Therefore we select proper initial conditions for the minimization process to obtain a ground state with a single DW in the middle of the chain.

Fig. 2.2 compares the ground state of the  $J_1$ - $J_2$  model, for which the spiral angle  $\phi_0$  is obtained from Eq. (2.7), and the ground state of the generalized model. The figure shows the dependence of the azimuthal angle of spins on the site number. We can compare the 2D solution from Eq. (2.1) with the 3D solution of the generalized model as we have

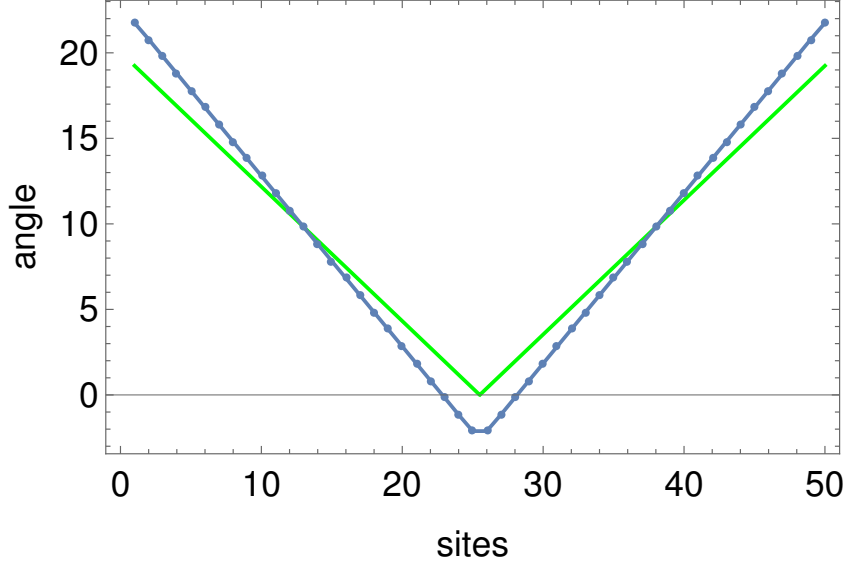


Figure 2.2: The profile of azimuthal angle of spins  $\phi_n$  at site  $n$  along the chain in presence of a DW. (green) angle profile computed within the  $J_1$ - $J_2$  model from Section 2.2. (blue) ground state of the general Hamiltonian (2.9). The V-shape in the center indicates the reversal of spin rotation sense due to the presence of a DW. The solution of the general Hamiltonian has a different slope due to the additional terms introduced in the model. The angle is expressed in radians and is not reported in modulus  $2\pi$  for a simpler visual comparison of the two solutions.

imposed the generalized spiral solution to lie in the  $ab$  plane through the anisotropy term in the Hamiltonian. The DM term couples the spins with the polarization, this causes the spiral pitch (rotation angle between the two adjacent spins) to be different from the  $J_1$ - $J_2$  case. The green curve corresponds to the spiral pitch  $\pm\phi_0$  (cf. Eq. (2.7)). The change of the slope in the V-shaped fashion is due to the presence of a chiral DW in the center of the chain. The DW connects two different chiral domains with the opposite spin rotation. This results in an increase or decrease, respectively, of the azimuthal angle in the two domains.

We point out that the increase of the azimuthal angle in the generalized solution is close to a perfect linear behaviour. The slight misalignment in the figure is a numerical effect. Inside domains spins rotate by the same angle, as the Hamiltonian 2.9 is translationally invariant, and a constant pitch is expected along the chain.

### 2.4.1 Modelling magnetic and electric susceptibilities

After introducing the model and describing the ground state of the system, we are now ready to perform an analysis of magnetic and lattice excitations in the spin spiral state.

We will utilize a method akin to the one used in Chapter 1: we start from the minimum of the Hamiltonian and we perform a second order expansion around the ground state, then we solve the associated eigenproblem to get the excitations. We use a different method to compute the response functions (electric, magnetic and ME susceptibilities). To show how to compute the susceptibility, we first consider a simple case: an electric charge  $q$  oscillating with a frequency  $\bar{\omega}$  around an equilibrium position ( $x_0 = 0$ ). An



external electromagnetic wave with frequency  $\Omega$  and electric field amplitude  $E$  is applied and interact with the charge. The motion happens along the  $x$  direction, aligned with the field,

$$m(\ddot{x} + \bar{\omega}^2 x) = qEe^{-i\Omega t}. \quad (2.12)$$

We Fourier transform the previous equation into

$$\int m(\ddot{x} + \bar{\omega}^2 x)e^{-i\omega t} dt = qE \int e^{i\Omega t} e^{-i\omega t} dt, \quad (2.13)$$

and, by integrating in  $t$ , we get

$$-\omega^2 \tilde{x} + \bar{\omega}^2 \tilde{x} = qE\delta(\Omega - \omega), \quad (2.14)$$

from which we obtain an expression of the Fourier transform of the displacement  $\tilde{x}$  as a function of the driving frequency  $\Omega$  and the Fourier frequency  $\omega$

$$\tilde{x}(\omega) = -\frac{qE\delta(\Omega - \omega)}{m(\omega^2 - \bar{\omega}^2)}. \quad (2.15)$$

In a crystal instead, the charges are arranged periodically and the electric polarization is defined as a density of electric dipoles. The dipole associated with the charge  $q$  is, in Fourier space,  $\tilde{d} = q\tilde{x}$ . It follows that the polarization  $\tilde{P}$  in Fourier space is

$$P(\omega) = \frac{q\tilde{x}(\omega)}{V}, \quad (2.16)$$

with  $V$  being the unit cell volume. Finally we can compute the electric susceptibility,

$$\alpha^e(\omega) = \frac{dP(\omega)}{dE(\omega)} = \frac{1}{V} \frac{q\tilde{x}(\omega)}{E(\omega)} = \frac{q^2}{mV(\bar{\omega}^2 - \omega^2)}, \quad (2.17)$$

where  $E(\omega) = E\delta(\Omega - \omega)$ . To summarize, electric susceptibility is proportional to the oscillating component of the polarization, induced by the external field,  $\alpha^e(\omega) \propto \tilde{P}(\omega)$ . In the following, we generalize this calculation to the case of the model we are studying. Despite the bigger complexity, the result still takes the form of a sum of Lorentzians, cf. Eq. (2.17), with the characteristic denominator, which for a static susceptibility  $\alpha^e(\omega = 0)$  is proportional to  $1/\bar{\omega}^2$ . Similar consideration can be repeated for the magnetic susceptibility, proportional to the oscillating component of the magnetization, and with the ME susceptibility, that depends on both the magnetization and polarization components.

## 2.4.2 Susceptibility from eigenmodes

To compute the susceptibility from the Hamiltonian, Eq. (2.9), we proceed in a similar way as in Chapter 1. We start by identifying a local minimum of the Hamiltonian in the spiral configuration with a DW in the center. For brevity, we introduce a generalized variable  $\boldsymbol{\xi}$ , so that  $\xi_i = (\theta_i, \phi_i, \boldsymbol{\pi}_i, \delta\mathbf{r}_i)$ . We call  $\boldsymbol{\xi}_0$  the values of variables in the ground state. We now introduce a small deviation  $\tilde{\boldsymbol{\xi}}$  so that, close to the ground state, we obtain  $\boldsymbol{\xi} = \boldsymbol{\xi}_0 + \tilde{\boldsymbol{\xi}}$ . As in Chapter 1, by substituting this expression for  $\boldsymbol{\xi}$  in  $H$  and taking derivatives up to the second order with respect to the different components of  $\tilde{\boldsymbol{\xi}}$ , we build a Hamiltonian matrix,

$$\mathcal{H} = \begin{pmatrix} \partial_{\phi\theta}^2 & \partial_{\phi^2}^2 & \partial_{\phi\pi}^2 & \partial_{\phi\delta r}^2 \\ -\partial_{\theta^2}^2 & -\partial_{\theta\phi}^2 & -\partial_{\theta\pi}^2 & -\partial_{\theta\delta r}^2 \\ -\partial_{\delta r\theta}^2 & -\partial_{\delta r\phi}^2 & -\partial_{\delta r\pi}^2 & -\partial_{\delta r^2}^2 \\ \partial_{\pi\theta}^2 & \partial_{\pi\phi}^2 & \partial_{\pi^2}^2 & \partial_{\pi\delta r}^2 \end{pmatrix} H, \quad (2.18)$$

from which it is possible to obtain the equations of motion for all the variables in a harmonic approximation.  $\partial_{xy}^2$  means that we are considering partial second order derivatives in the variables  $x$  and  $y$ . We omit the  $\sim$  for simplicity of notation. The minus sign is due to the relation of conjugation between the two couples of canonic variables,  $(\delta\mathbf{r}, \boldsymbol{\pi}), (\theta, \phi)$ , while the form of the matrix is chosen so that the Hamilton equations can be rewritten in the compact form:

$$\dot{\boldsymbol{\xi}} = \mathcal{H}\boldsymbol{\xi}, \quad (2.19)$$

where here  $\boldsymbol{\xi}$  absorbs the  $\sin\theta_i$  terms that would be required as in Eq. (1.7). In Fourier space, we obtain an equivalent to an eigenvalue problem

$$\mathcal{H}\boldsymbol{\xi} = i\omega\boldsymbol{\xi}. \quad (2.20)$$

As stated in the previous section, we need the Fourier transform of polarization and magnetization to compute the susceptibilities of the system. In Section 2.2 we discussed how the spiral periodicity is in general incommensurate with the lattice. The absence of an exact periodicity makes difficult the use of an analytical Fourier transform. To obtain the quantities needed for the computation of susceptibilities, we compute eigenvectors and eigenvalues of  $\mathcal{H}$  in real space. In order to obtain the polarization in Fourier space we perform a discrete Fourier transform on the components of  $\boldsymbol{\xi}$ , that are related to the electric polarization

$$\mathbf{P}(k, \omega) = \sum_n^{N-1} Z\delta\mathbf{r}_n(\omega)e^{i\frac{2\pi}{N}kn}, \quad (2.21)$$

where  $N$  is the total number of spins in the chain. Note that  $\delta\mathbf{r}$  is a function of  $\omega$ , because  $\boldsymbol{\xi}$  is a solution of Eq. (2.20).

In order to obtain the Fourier transform of the magnetization we first expand it to the first order in the components  $\tilde{\theta}$  and  $\tilde{\phi}$  of  $\boldsymbol{\xi}$  around the ground state:

$$\mathbf{M}_i = g\mu_B \left( \mathbf{S}(\theta_{i0}, \phi_{i0}) + \frac{d\mathbf{S}(\theta_{i0}, \phi_{i0})}{d\theta_i} \tilde{\theta}_i + \frac{d\mathbf{S}(\theta_{i0}, \phi_{i0})}{d\phi_i} \tilde{\phi}_i \right), \quad (2.22)$$

where  $\mathbf{M}_i$ ,  $\theta_i$  and  $\phi_i$  are all functions of  $\omega$ . The discrete Fourier transform of the magnetization is then

$$\mathbf{M}(k, \omega) = \sum_n^{N-1} \mathbf{M}_n(\omega)e^{i\frac{2\pi}{N}kn}. \quad (2.23)$$

In the previous section we showed that, in Fourier space, the electric susceptibility is proportional to the oscillating component of the polarization. A similar argument can be made for the magnetic susceptibility. Fig. 2.3 shows the electric and magnetic susceptibilities computed from Equations (2.21) and (2.23). It is possible to see the effects of ME coupling by looking at the different components of the electric and magnetic susceptibilities. There is a close resemblance between components  $\alpha_{11}^m$  (or  $\alpha_{22}^m$ ) magnetic susceptibility with component  $\alpha_{33}^e$  of the electric one. This is due to the particular shape of the DM interaction, which couples only perpendicular components of magnetization and polarization. For the same reason,  $\alpha_{11}^e$  resembles  $\alpha_{33}^m$ . Instead,  $\alpha_{22}^e$  only has one single mode and does not resemble any other component of the susceptibility. This is due to the vector  $\mathbf{r}_{12}$  in the DM term being parallel to the  $b$  axis. There is no coupling with the polarization along that direction hence the associated components of the susceptibility are zero.

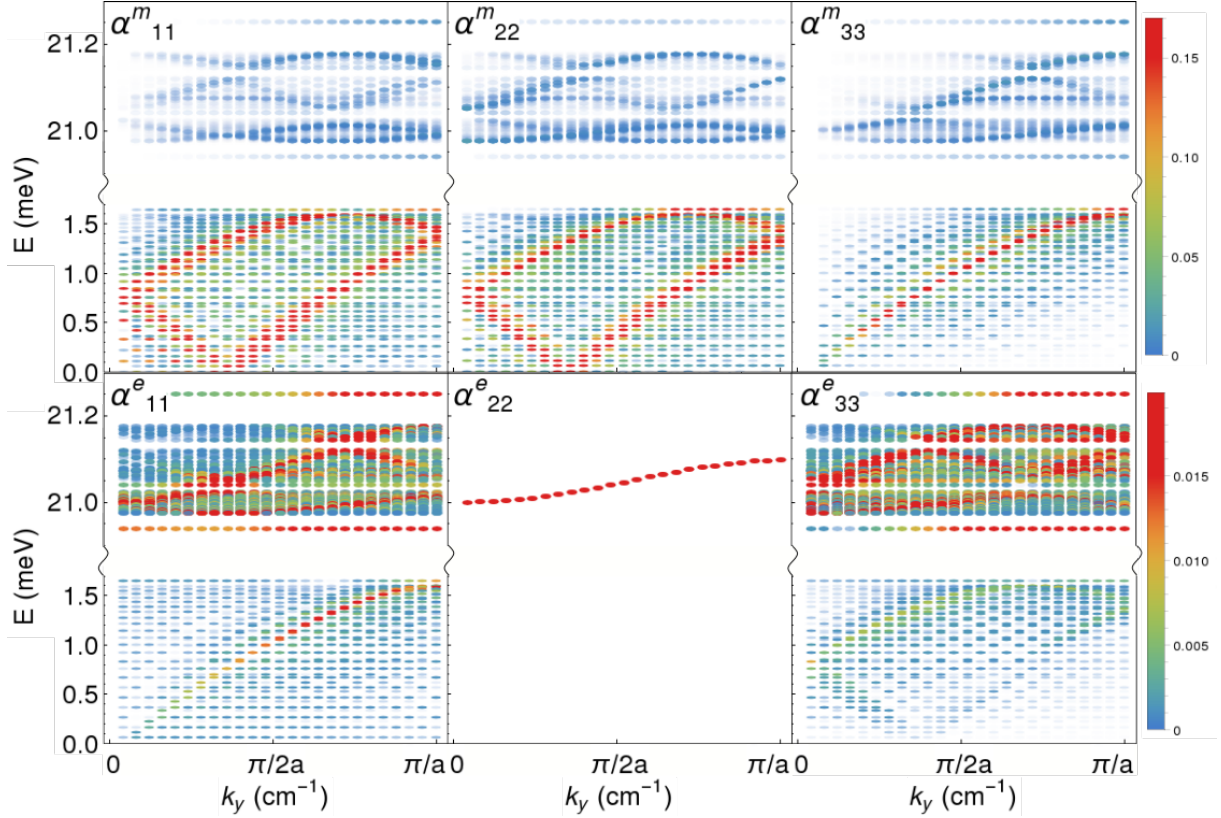


Figure 2.3: Diagonal components of magnetic (top row) and electric (bottom row) susceptibility tensors, computed in a spiral state with a DW. Colorscale encodes the intensity of the signal in arbitrary units. An energy cut is made in the graphs between 1.6 and 20 meV as there are no excitations in that range. Excitations below the energy cut originate from acoustic magnons while the excitations above are related to polar modes. Similarities between components 11, 22 of magnetic (electric) susceptibility and component 33 of electric (magnetic) susceptibility are present and are due to the ME coupling in the form of DM interaction.

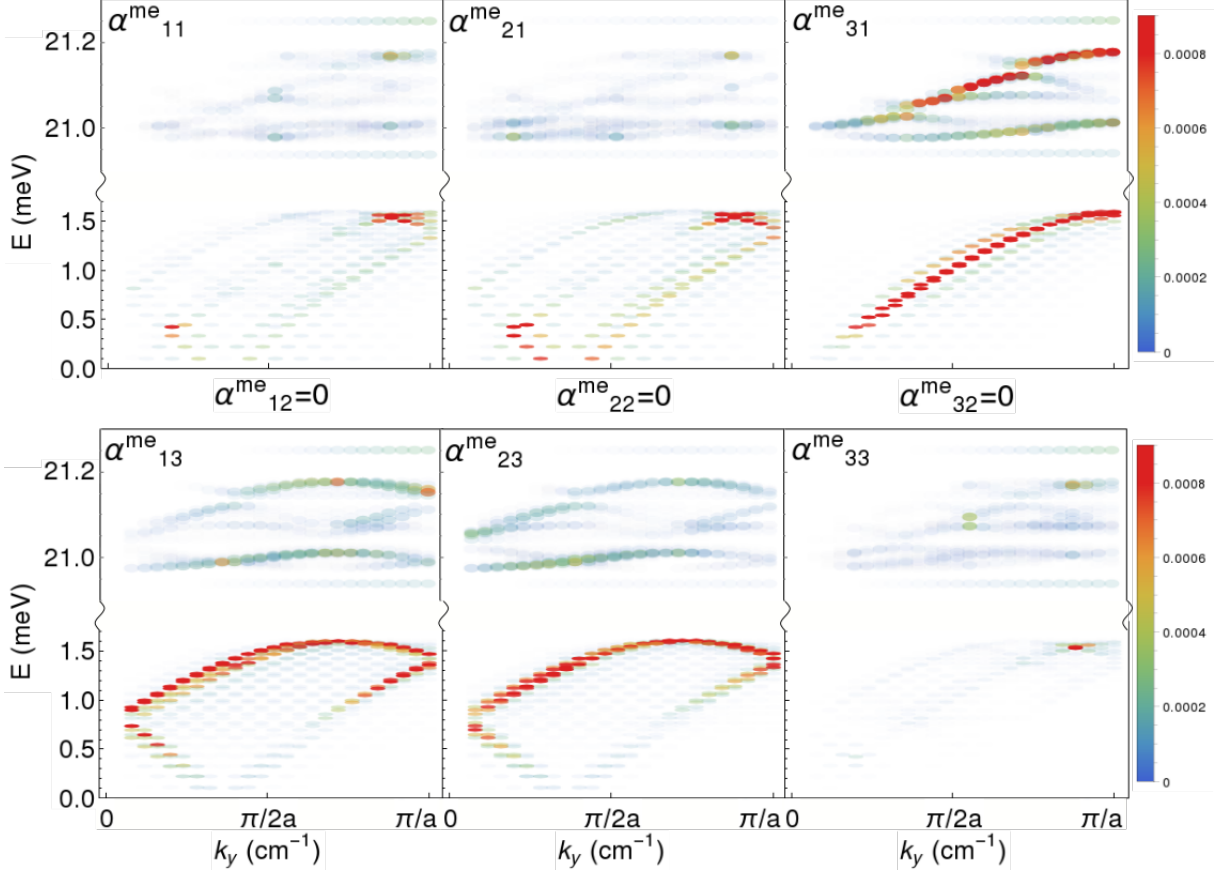


Figure 2.4: Magneto electric susceptibility computed with Eq. (2.24). Colorscale encodes the intensity of the signal in arbitrary units. All components  $\alpha_{i2}^{\text{me}}$  are zero due to the particular shape of ME coupling, discussed in the text.

We can distinguish in the susceptibilities two kinds of excitations: low energy ones which are more intense in the magnetic susceptibility, and high energy ones which are more intense in the electric susceptibility. Low energy modes are “acoustic” magnetic modes while high energy ones are “optic” polar modes. The fact that they are present in both magnetic and electric susceptibility is again due to the ME coupling.

We can compute the resonant part of the ME susceptibility  $\alpha^{\text{me}}$  from the magnetization  $\tilde{M}$  and polarization  $\tilde{P}$  of every mode. It is possible to show that, with spin and polar mode damping neglected, the  $\alpha^{\text{me}}(\omega, q)$  is related to the magnetization and polarization profiles of the mode, or more precisely, to their Fourier components at the wave vector of the external probe field,  $\tilde{M}(\omega, k)$  and  $\tilde{P}(\omega, k)$ , as the product of the two

$$|\alpha^{\text{me}}(\omega, k)| \propto |\tilde{M}(\omega, k)\tilde{P}^*(\omega, k)|, \quad (2.24)$$

Fig. 2.4 reports the ME susceptibility, where all the terms  $\alpha_{i,2}^{\text{me}}$  are zero due to the peculiar ground state we are analyzing. The spiral is confined into the  $ab$  plane and the wave vector  $k$  being parallel to  $\hat{y}$  causes the spin deviations to not couple to the polarization  $P_y$  through the DM term. Thus the term  $\mathbf{r}_{12} \times \delta\mathbf{r}_i$  has  $\mathbf{r}_{12} \parallel \hat{y}$ , which enforces the shifts  $\delta\mathbf{r}_i$  to be bounded into the  $ab$  plane. It follows that DM interaction couples the spin deviations only to the polarization in the spiral plane, thus leading to zero  $\alpha_{i,2}^{\text{me}}$  terms of the ME susceptibility.

## 2.5 Role of the domain wall

Throughout the course of the present chapter we described how a spiral solution arises from the generalized Hamiltonian, Eq. (2.9), and how to extract information about the electric and magnetic responses through the calculation of susceptibilities. We also mentioned that the solution that we studied, as well as the real material that we are modelling, is characterized by the presence of chiral domains and the DWs between them. In this section we are going to describe in detail the effect of a DW on the dynamics of the excitations in the material. With the presence of a DW, new sliding and twisting modes are possible in the spectrum. As the DW is not pinned, this results in low frequency modes. The presence of DW broadens magnons that, in a pure cycloidal configuration, would be sharp. A coupling between DW-localized modes, and the bulk ones, potentially allows for the access and manipulation of these otherwise unreachable modes.

The presence of DW-localized modes is a crucial feature of the system we are studying. The DW acts as a barrier and as region of separation between two chiral domains. When a perturbation of any kind (i.e. thermal fluctuations, external fields, excitations...) acts on the domains and changes their shape or volume, there are repercussions on the DW.

This kind of phenomena is described through DW-related modes. For example, if one domain grows in size while the adjacent one shrinks, the DW wall between them will move, which is described by a DW sliding mode. Another possible DW-localized mode is a DW breathing mode, that represents the oscillations of the DW width. Other less intuitive DW-related modes exist. For example, an excitation of a breathing mode of a head-to-head wall will be accompanied by surface charge oscillations at the wall. In an analogous manner, magnons can interact with the wall, scattering off it, pushing or twisting the wall.

With these premises is it possible to realize the importance of a ME coupling for the DW-related modes. As discussed in Section 2.3, the DM interaction induces a ME coupling of magnetic and electric degrees of freedom (spins and polarization). The immediate consequence of this coupling is the mixing between polar modes and magnons and the possibility to dynamically control e.g. magnetic excitations with electric fields or vice versa.

We are interested in magnons that can be excited with the electric field, which we refer to as electromagnons [20]. In particular, an electromagnon is a hybrid magnon-phonon excitation that can be excited with a long-wavelength electric field (e.g electric field of light or of an oscillating electric dipole). Fig. 2.5 gives an example of a high-energy hybrid magnon-phonon mode. This particular mode is not localized at the wall. Nevertheless, the spin and polarization textures at the DW enter the equations of motion for magnons, and create a potential that may scatter magnons and preclude their propagation from one domain to another. This could be consistent with the mode amplitude in Fig. 2.5 having a node at the DW. In fact, in this particular mode the oscillations of spins and electric dipoles near the wall are diminished.

Interesting DW-localized modes can be found at the lowest frequencies, as seen in Fig. 2.6. In particular, Fig. 2.6 (a,b) shows DW-localized modes with the polarization profile that are even with respect to the position of the wall. These modes mix with even bulk magnons. The overall action of these modes is that of a sliding of the DW. The peak results from subtracting the polarization profiles of two DWs, shifted with respect to each other by a small distance,

$$\delta P(x) \sim \tanh(x + \delta)/\lambda - \tanh x/\lambda. \quad (2.25)$$

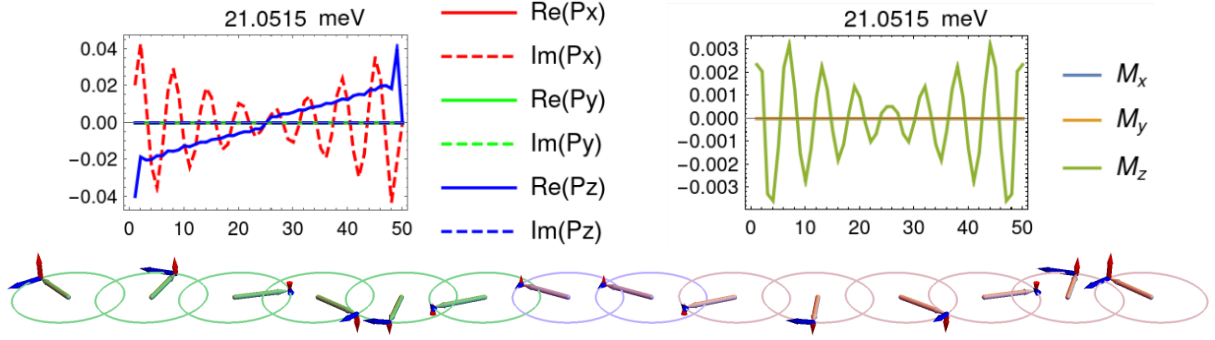


Figure 2.5: (Top row) Oscillating ferroelectric polarization profile (left) and spin deviations (right) for the excitation at  $E \sim 21$  meV. On the  $x$  axis is the site number and on the  $y$  axis the oscillation amplitude (a.u.). In this particular mode only  $\text{Im}[P_x]$  and  $\text{Re}[P_z]$  are non-zero while only  $M_z$  is non-zero in the magnon part. The resemblance of  $M_z$  to  $\text{Im}[P_x]$  is due to the DM interaction. (Bottom row) visual representation of the spin deviations induced by the mode. Green and orange arrows represent spins belonging to different chiral domains, while purple spins are at the DW. Red and blue arrows represent tilting of spins induced by the mode. Arrows are magnified for better visualization. The decrease of arrows near the wall shows that the mode does not affect the DW.

The DW wall is ferroelectric, thus the mode changes the electric polarization and is, in fact, an electromagnon. The bands of such low-energy hybridized modes are present in the lower part of the spectrum, seen in Fig. 2.3, and describe wall sliding at  $k = 0$  and DW wobbling at  $k \neq 0$ . The magnons with an odd polarization, as seen in Fig. 2.6(c-d), are practically unaffected by the presence of the DW.

The interaction between DW-localized modes and bulk modes paves the way for possible DW-based technology. DWs could act as filters or gates for certain modes, blocking or allowing their propagation. Moreover, due to ME coupling, DW manipulation could help access otherwise unreachable bulk modes.

The frequencies of the modes may be overestimated, since DWs in our simulations were rather narrow, owing to a strong hard axis anisotropy. In  $\text{TbMnO}_3$  and in general in other spiral magnets, the electromagnon is much softer. A soft electromagnon leads to a large contribution to the static dielectric constant of the material  $\epsilon = 1 + 4\pi\alpha^e$ . In fact the electric susceptibility at zero frequency is, from Eq. (2.17),

$$\alpha^e(0) = \frac{q^2}{mV\bar{\omega}^2}, \quad (2.26)$$

which is large for soft modes ( $\bar{\omega} \rightarrow 0$ ). This is a possible explanation for the enhancement of the dielectric constant in MHz range in spin spiral systems [31, 32]. Domain walls have already been blamed for the dielectric constant enhancement in a proper ferroelectric: rhombohedral  $\text{BaTiO}_3$ , where it appears in the vicinity of the Bloch- to Ising-type DW phase transition [33], where a polar DW-localized phonon softens near such transition.

### 2.5.1 Effects of DWs on the excitation spectrum

The presence of a DW in the spin spiral order does not only introduce a different kinds of DW-related modes (i.e. DW sliding, breathing, tilting), but it also affects the shape of the magnon bands. The susceptibility of a single-domain spin spiral state only contains

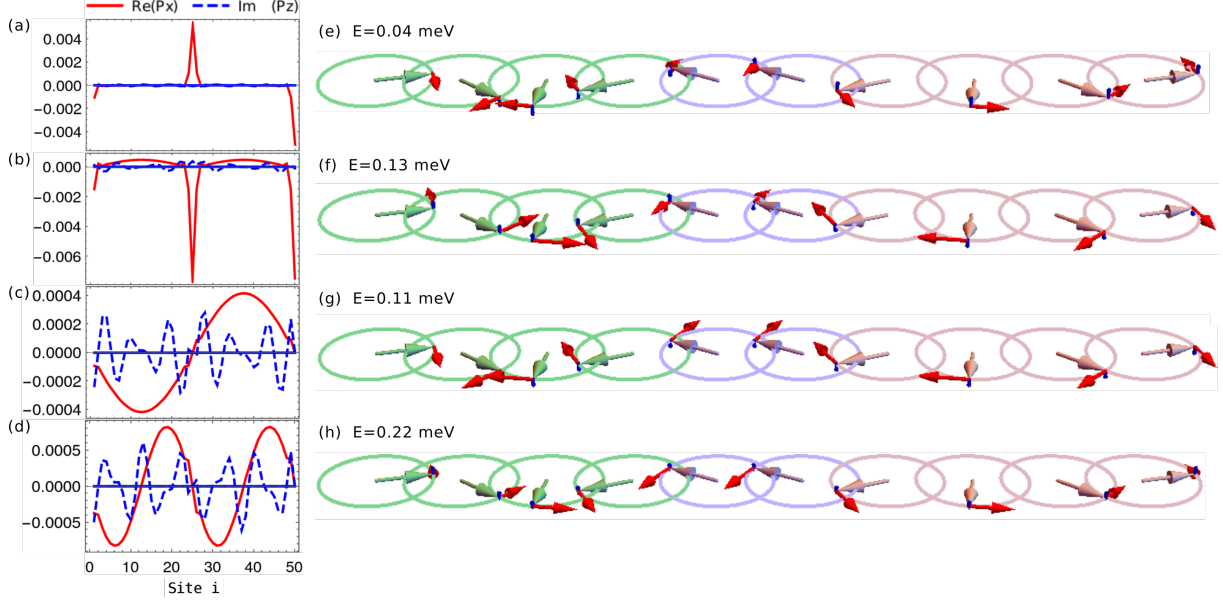


Figure 2.6: Soft modes, localized at the chiral DW. (a-b) Non-zero polarization components of the lowest-energy modes. These even modes are a mixture of DW sliding and bulk modes. Site number is reported on the horizontal axis and the polarization profile of the modes in arbitrary units is on the vertical axis. (e-f) Spin deviations corresponding to the modes shown in (a-b). The energies of the modes are indicated by the labels. Spins in green and orange belong to domains of opposite chirality, while purple spins are localized at the wall. In-plane spin deviations are indicated by red arrows, tangent to the circles, and the (much smaller) perpendicular components are in blue. (c-d) DW-odd bulk modes with a node at the DW position. This symmetry causes the modes to not mix with the DW-localized modes (sliding and tilting). (g-h) are the corresponding spin deviation.

sharp bands, both for magnetic and electric excitations due to translational symmetry, as seen in Fig. 2.7 [34]. In contrast, Fig. 2.3, shows the spectrum of spiral state with a chiral DW. The magnon bands are broadened due to the scattering of the wall.

In Fig. 2.8 we report the electric susceptibility ( $\alpha_{11}^e$ ) of two spiral configurations, with and without the DW. The presence of the DW breaks the translational symmetry and broadens the bands, localizing the modes in one or another particular domain or, in the case of DW-localized modes, in the proximity of the DW. This broadening of the modes makes it easier to excite some of them. The broadening occurs for both acoustic (magnons) and optical (lattice) modes but its contribution is of greater importance in the acoustic part as the excitations of the wall are mostly low-energy ones. The consequent broadening of the polar modes is due to the DM interaction that mirrors for polar modes the broadening of the magnons.

## 2.6 Conclusions

This chapter has been devoted to the study and characterization of a most basic non-collinear spin configuration, the spin spiral. The importance of such a state is both due to the unique modes that a spin spiral configuration naturally hosts, and to the presence of DWs in the spiral. In particular, the presence of DWs enriches the spectrum with new modes, domain-confined or DW-localized modes. DM interactions tie the spin rotation



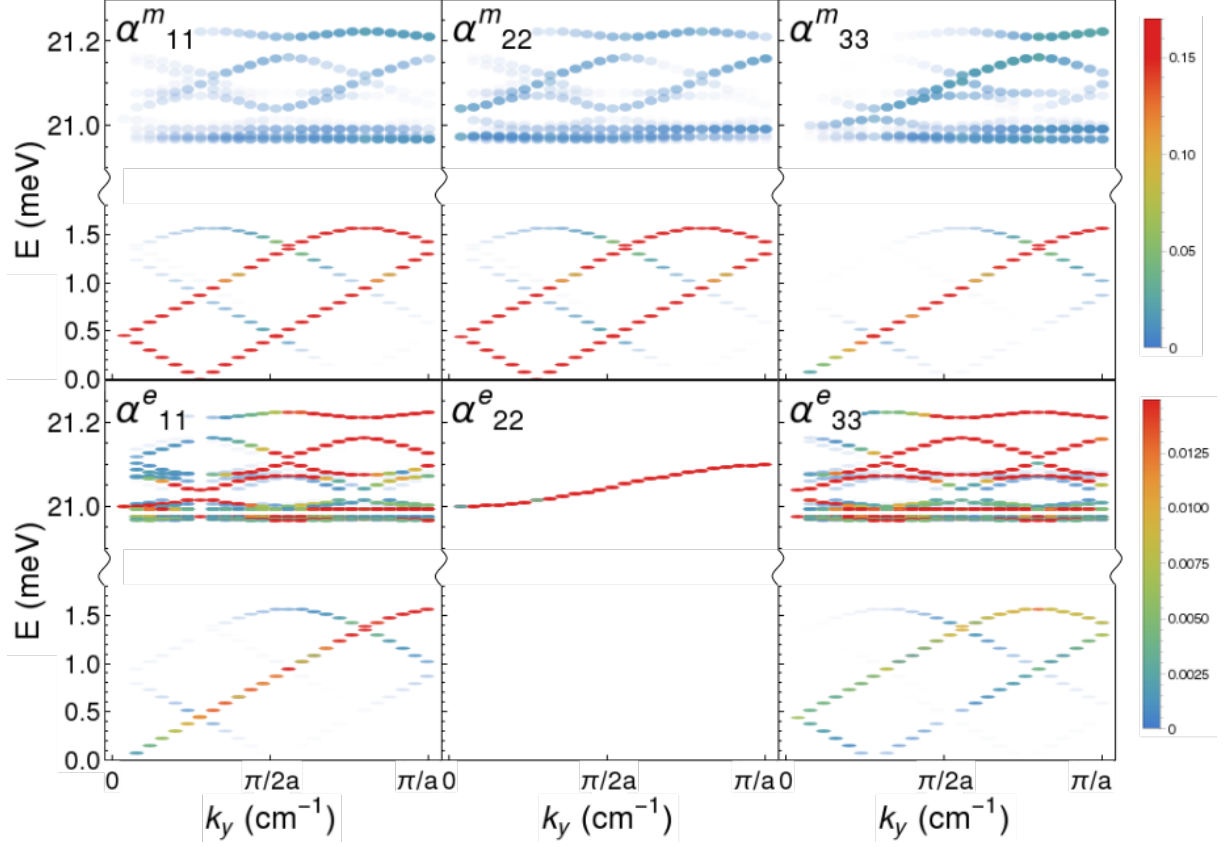


Figure 2.7: Magnetic (top) and electric (bottom) susceptibilities for a pure spiral. In absence of DW the excitations are delocalized along the whole spiral, resulting in sharp lines in the Fourier space. An energy cut along the y-axis is made due to absence of any modes in the removed region.

sense (spin chirality) to the ferroelectric polarization. Therefore chiral DWs in cycloidal spiral magnets are also ferroelectric.

The main findings of this chapter are in the description of hybrid magnons and phonon excitations that are mixed by the DM interactions. Particularly, a soft DW localized sliding mode is identified as an electromagnon. This suggests that the dielectric constant may be tuned via changing DW density, for instance, through poling. This could pave a way to the new types of tunable dielectrics. The interplay of magnetic and electric degrees of freedom, coupled with the presence of DWs, contributes to explain the presence of high-valued dielectric constants in real materials that host spin order akin to the spiral system we discussed. A study of the ME effect has been carried out. Unique modes related to the presence of the DW have been identified, that mix bulk modes with DW-localized ones, opening the way for the manipulation of bulk modes through DW interaction.



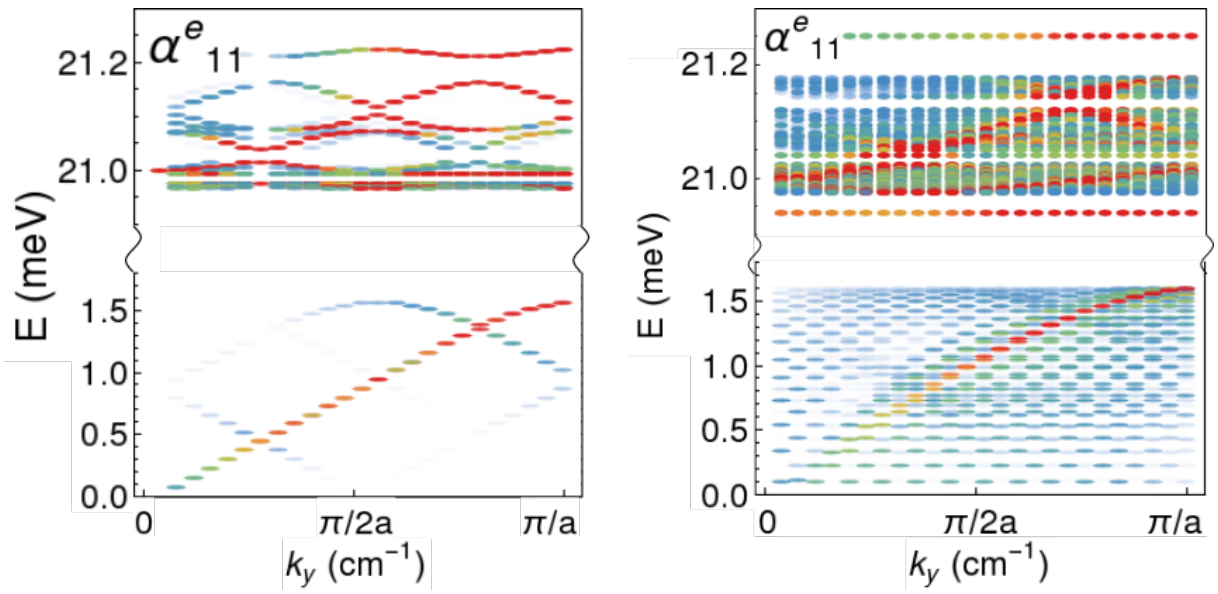


Figure 2.8: Comparison of electric susceptibility component  $\alpha^e_{11}$  for (left) a single-domain spiral state and (right) a spiral state with a DW in the center. Both acoustic, primarily magnetic, and optical modes, lattice modes, are broadened due to the presence of the DW. An energy cut along the y-axis is made due to absence of any modes in the removed region.

# Chapter 3

## Magnetic excitations and skyrmion dynamics in $\text{GaS}_4\text{V}_8$

### 3.1 Introduction

In the previous Chapter we described the peculiar spiral order originating from frustrated exchanges. This Chapter makes use of a fairly general model, not too different from the models in chapters 1 or 2, but with all exchanges being ferromagnetic. Remarkably, as we will see, the Hamiltonian results in spiral and even skyrmionic lattice states at non-zero temperature. To simulate these states and their dynamics we make use of Monte-Carlo simulations in combination with the Landau-Lifshitz-Gilbert (LLG) dynamics, capturing the dynamics of the spin texture that characterizes the system. This allows for additional insights into thermal conductivity and photoexcited dynamics in the materials as described by this rather general model. This approach makes it possible to reproduce the experimentally measured thermal conductivity and transient magnetization oscillations seen in ultrafast optical experiments [35].

The material that we study in this Chapter is  $\text{GaV}_4\text{S}_8$  (GVS), a multiferroic semiconductor of recent interest belonging to the lacunar spinel family that hosts a fascinating phase diagram. For different temperatures and external magnetic fields, cycloidal (Cyc), skyrmionic (SkL) and ferromagnetic phases are observed [36]. This rich phase diagram motivates the study of GVS because when a peculiar spin order is present the response of spin excitations to external perturbations (e.g. to photoexcitations, strains, and external electric and magnetic fields) is altered significantly. GVS, which can easily switch between different phases, provides a powerful test-case to study the general behaviour of excitations on the background of really diverse magnetic orders.

This Chapter is structured in the following way: we start by discussing the recent literature on GVS, describing the material and providing an explanation on how the phase diagram arises. We then focus on the recent experimental work of our collaborators (group of Paul H.M. van Loosdrecht, Univ. of Cologne), with particular attention on time-resolved magneto-optical Kerr effect (trMOKE) measurements on GVS. This will serve as a starting point for our theoretical description and simulations. Finally, we discuss the results of our simulations that address coherent collective modes and thermal conductivity, inferred from the magnetization recovery following transient photoexcitation. The aspects in which simulations agree with the experimental results are outlined, and the reasons behind the discrepancies are discussed.

## 3.2 The material

$\text{GaV}_4\text{S}_8$  (GVS) is a multiferroic semiconductor of the lacunar spinel family [37, 38]. It exhibits cubic non-centrosymmetric structure at room temperature 3.1, while at 42 K [39] a transition to a polar rhombohedral structure occurs. In comparison with the common spinel structure  $\text{AB}_2\text{X}_4$ , the fundamental unit of  $\text{GaV}_4\text{S}_8$  has one Ga for every two positions, resulting in an alternating Ga not-Ga structure. This defect causes a non uniform distribution of the  $\text{V}_4$  atoms that arrange in alternating larger and smaller tetrahedra [40]. The  $\text{V}_4$  tetrahedra, that are arranged in a face-centered cubic lattice, are responsible for the magnetic properties of GVS as the molecular orbitals of  $\text{V}_4\text{S}_4$  each host a spin-1/2. In this configuration a magnetic easy axis anisotropy is observed along the  $[111]$  direction [36, 41] of the cubic  $\text{V}_4$  lattice. Along this direction a Jahn-Teller distortion is responsible for the transition from cubic to rhombohedral.

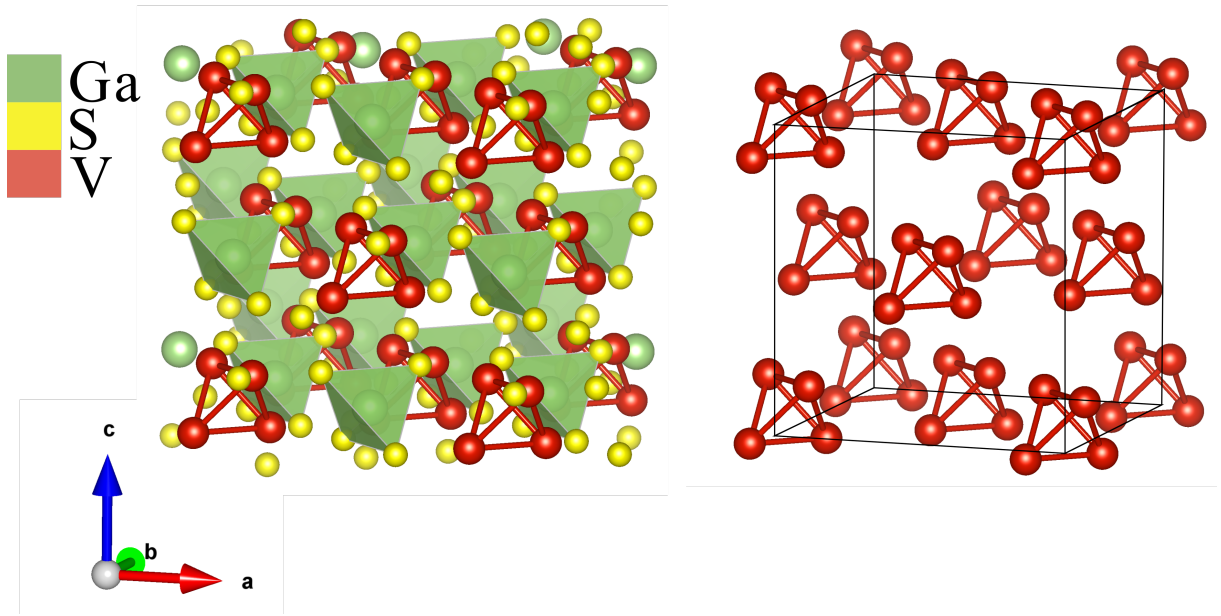


Figure 3.1: Cubic phase of  $\text{GaV}_4\text{S}_8$ . Comparative visualization of GVS structure (left) with the  $\text{V}_4$  cubic lattice (right). Solid lines in the cubic in  $\text{V}_4$  lattice are a guide for the eye.

In its rhombohedral phase GVS has been observed to have interesting magnetic properties. In fact, below the Curie temperature of 13 K [41], the phase diagram of GVS features a rich plethora of magnetic phases, as shown in Fig. 3.3. Below the Curie temperature the system displays either a ferromagnetic phase (FM), Néel-type skyrmion lattice phase (SkL) or a cycloidal phase (Cyc). In the Néel-type skyrmion, spins rotate around radial planes (Fig. 3.2) along the radial direction. It is possible to rationalize the appearance of different phases of the phase diagram in terms of general energy considerations. Let  $F$  be the free energy of the system,

$$F = E - TS, \quad (3.1)$$

where  $E$  is the total energy,  $T$  the temperature and  $S$  the entropy of the system. The entropy contribution is null at  $T = 0$  or negligible at low temperatures. The dominant interaction being the FM Heisenberg exchange  $J\mathbf{S}_1 \cdot \mathbf{S}_2$ , with  $J < 0$ , between nearest neighbor spins  $S_1$  and  $S_2$  results in a FM state. As the temperature is increased, the FM phase, where spins have maximal exchange field from the neighbors and thus form

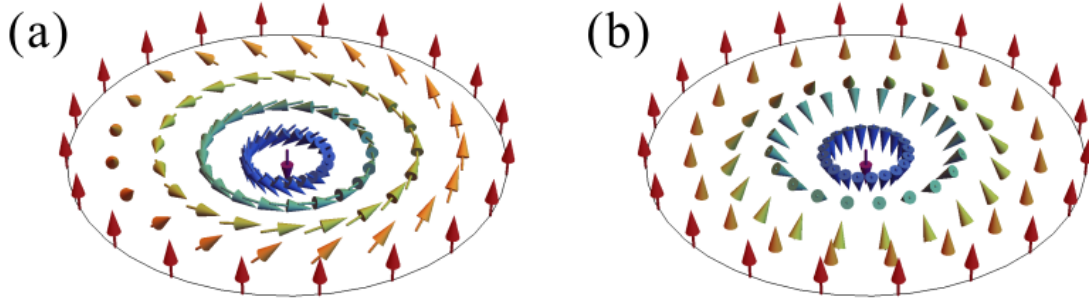


Figure 3.2: (a) Bloch type skyrmion: the spins rotate perpendicular to radial directions. (b) Neel type skyrmion: the spins rotate along the radial direction.

hard magnons, becomes less favorable compared to the spiral state, in which the canted neighboring spins produce lower exchange field. This is due to the free energy gain on the entropic term in non-collinear states like Cyc or SkL, where non-collinearity of the neighbors results in a lower effective field and hence softer magnons. To illustrate this statement, we consider a mean-field decoupling  $J\mathbf{S}_1 \cdot \mathbf{S}_2 \rightarrow J\mathbf{S}_1 \cdot \langle \mathbf{S}_2 \rangle$ , and compute the entropy of spin  $\mathbf{S}_1$  in the effective magnetic field  $\mathbf{H} = J\langle \mathbf{S}_2 \rangle$ . This results in, up to a constant,

$$\mathcal{S} = \log \left[ \frac{\sinh x}{x} \right] - x \coth x, \quad x = \frac{HS_1}{T}. \quad (3.2)$$

Thus the entropy is a monotonically decreasing function of  $S_1 H/T$ . This reflects larger gain of the free energy on  $-T\mathcal{S}$  term in a spiral phase with softer magnons, compared to the ferromagnetic phase with harder magnons. Eq. (3.2) is derived in appendix C. The presence of an external magnetic field  $\mathbf{H}_{\text{ext}}$  introduces a Zeeman term in the free energy,

$$E_Z = -\mathbf{M} \cdot \mathbf{H}_{\text{ext}} \quad (3.3)$$

where  $\mathbf{M}$  is the magnetization. Even at higher temperatures and for non-collinear states, the presence of the Zeeman term requires the average magnetization of the phase to be aligned with the field. For low fields at sufficiently high temperatures, the system undergoes a phase transition from FM to Cyc, exhibiting a phase with zero average magnetization at zero field. Thus, Cyc does not gain energy linearly on the Zeeman term. However, it has a larger entropy contribution than FM, as well as a large contribution from the DM interaction due to the rotation of the spins. In fact the energy due to DM interaction  $\sim \mathbf{S}_1 \times \mathbf{S}_2$  is zero for the FM phase while it has a finite value in the Cyc phase. Higher values of the field will ultimately dominate over the entropy term, bringing the system back to FM even at high temperatures, but before that an intermediate SkL phase is stabilized. The SkL phase can be considered as a FM phase with isolated magnetic bubbles dispersed through it. Therefore the overall magnetization value is close to that of the FM phase, as favored by the Zeeman term. However, the inner structure of the skyrmions allows an energy gain thanks to the DM term and the entropy term.

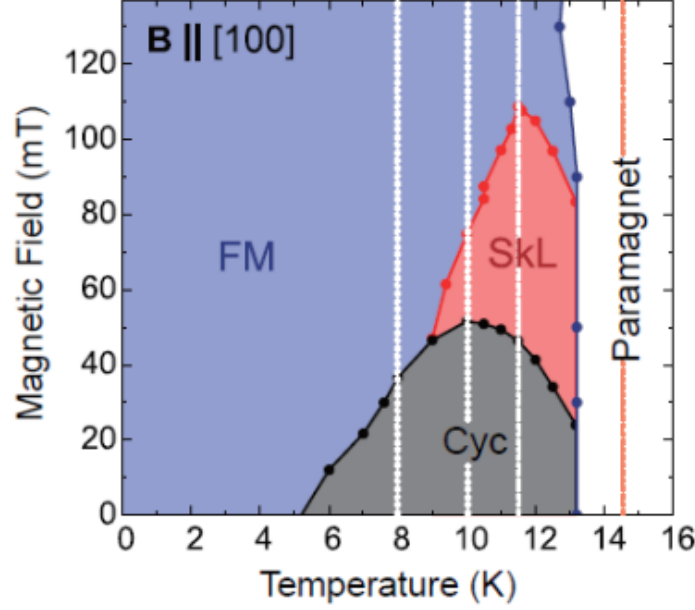


Figure 3.3: Phase Diagram of GVS in an external magnetic field applied along the cubic [100] direction. The vertical line at 10 K indicates the conditions of the measurements, that we interpret in the sections 3.2.1 and 3.4. Data from [35].

### 3.2.1 Experimental data

In this Chapter, the motivation for the analysis of the properties of GVS came from an experimental study of the material via time-resolved magneto-optical Kerr Effect (trMOKE, a review: [42]). When light is reflected from a magnetized surface, the intensity and polarization of the reflected beam changes due to the presence of the magnetization. Thus, by analyzing the reflected light from a material, it is possible to characterize its magnetization texture.

Besides being a non invasive and powerful tool to provide a detailed description of the magnetic properties of GVS, trMOKE is also ideal to study the response of the system to photoexcitations. Spins interact with the electromagnetic field of light: a spin in a magnetic field is subject to precession. In fact, a precession of the magnetization is observed in GVS as a consequence of photoexcitation. Additionally an excitation of skyrmion breathing modes [43] is observed, opening an interesting opportunity to study skyrmion dynamics. These studies lay the groundwork for a better comprehension, and ultimately a realization, of skyrmion-based devices. Furthermore, once the system is excited it is possible to study the thermalization process, which offers the possibility to comprehend how the various degrees of freedom (i.e. electrons, spins and the lattice) interact and exchange energy, how the excitations scatters and what role the background magnetic structure plays in the dynamics of these entities.

Fig. 3.4 shows trMOKE data [44] at 10 K, while the external magnetic field runs from 30 to 120 mT, spanning through the Cyc, SkL and FM phases as seen in Fig. 3.3. The figure represents the measured change in the polarization of light after it reflects on the magnetized surface of GVS. The phase of the reflected light changes after the reflection on a magnetized surface and is directly proportional to the magnetization of the material. When magnetization changes due to photoexcitation, the change is observed in the phase

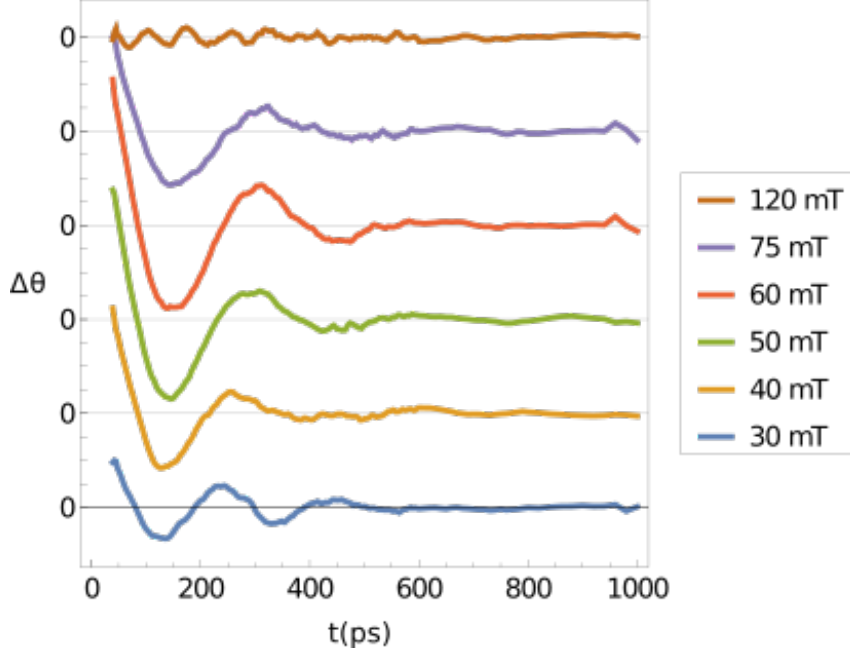


Figure 3.4: Experimentally observed coherent oscillation of the magnetization component along the direction of the external magnetic field [44]. The polarization change ( $\Delta\theta$ ) in the reflected light is directly related to the magnetization inside the material. Measurements are taken at 10 K, different magnetic fields (highlighted with different colors) are applied to select different phases along the phase diagram. Plots are rescaled vertically, horizontal lines added for reference

of the reflected light. A damped mode with frequency in the GHz range is visible from the experiment. The oscillation of the magnetization can be interpreted as the result of coherent spin precession around the direction of the external magnetic field. The observed modes have been excited through interaction with the light. It has been suggested earlier [35], that such a coherent spin precession may be triggered by a photo-induced quench of the anisotropy .

This response arises from the competition between external magnetic field and anisotropy. Let  $\mathbf{a}$  and  $\mathbf{b}$  be the unitary vectors in the direction of the magnetic field and the anisotropy, respectively. In the equilibrium state, the preferable spin direction will be some intermediate direction between the direction of the field and the anisotropy, i.e.  $\alpha\mathbf{a} + \beta\mathbf{b}$ . The magnitude of the coefficients  $\alpha$  and  $\beta$  depends on the strength of the two competing terms. If a sudden quench of the anisotropy happens, a new direction  $\alpha'\mathbf{a} + \beta'\mathbf{b}$ , with  $\alpha' > \alpha$  and  $\beta' < \beta$ , is preferred and therefore spins tilt more towards the direction of the magnetic field. The perturbation of the spin order forces a magnetization precession around the axis of the field, thus exciting the magnons responsible for the precession. As time passes, the energy pumped into the system through photoexcitation gets transferred to the rest of the material through magnon-phonon coupling, re-establishing the local equilibrium before the excitation, and bringing the magnetization back to the initial state. The time necessary for the magnetization to be restored to the initial value (recovery time) has also been measured and is shown in Fig. 3.5, and is directly related to the thermal conductivity of GVS.

As it is evident from Fig. 3.5, different phases correspond to different recovery times, and thus to different thermal conductivity values. The reason behind this difference

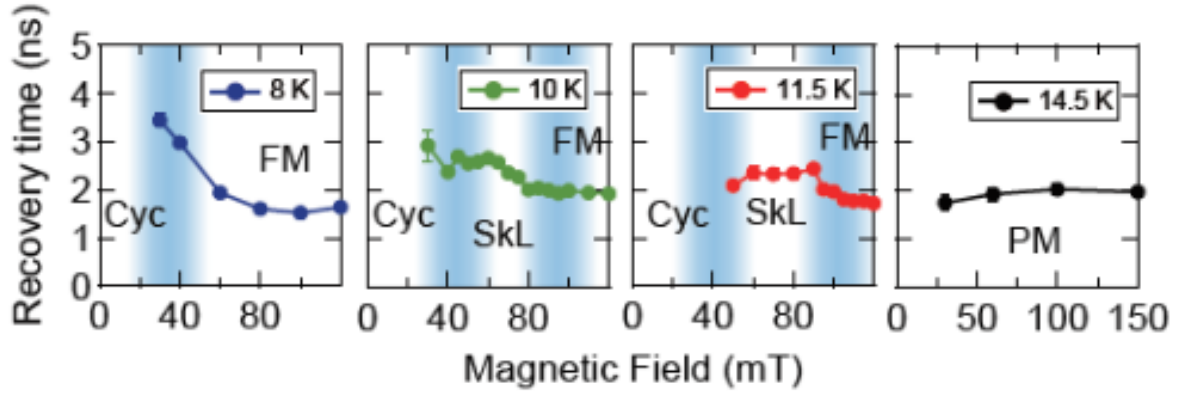


Figure 3.5: Recovery time in GVS measured for different temperatures [44]. After the photo-excitation, the material relaxes to the previous value of the magnetization, the recovery time differs from phase to phase.

lies in the mechanism of thermalization, i.e. the transfer of energy through magnon-phonon coupling and the scattering of magnons along the magnetic texture of the material. Fig. 3.5 shows that the Cyc and SkL phases have higher recovery time, i.e. lower thermal conductivity, than the FM and paramagnetic phases. This is due to the magnon scattering.

The photoexcitation induces magnetic excitations in the system. The excess energy stored in the magnons is then distributed to the rest of the system via thermalization. Therefore the magnon scattering plays a major role in this.

When the heat that has been introduced in the system from the photoexcitation is carried away by the magnons the magnetization returns to its initial value. For this to happen, magnons need to efficiently carry away the heat from the excited region. The ability to transfer heat away from the excited region is related to the mean free path of magnons. For example, a magnon that scatters off a magnetic defect exchanges heat at the scattering site, exciting another magnon or eventually transferring energy to the lattice. If the magnetic defect is close to the excited region, the local temperature does not decrease significantly, and the thermalization process requires more scattering events to dissipate the heat. To summarize, if magnons scatter more, their mean free path is lower, and thus the thermalization is slowed down. This happens in the Cyc and SkL phases due to the complex magnetic order of the structures. As we discuss in the following, upon the transition to the Cyc phase abundant chiral DWs appear which likely limits the magnon mean free path.

In the Cyc phase the spins arrange into a cycloidal configuration, but it is common for DWs to arise at the phase transition. These DWs separate regions where the cycloidal order is different, e.g. the spin rotation verse or the direction of the wave vector are different. DWs are objects whose presence alters the magnetic properties of the material and hence the magnon dynamics. In this scenario they act as magnetic defects that scatter magnons. The great number of DWs in the cycloidal phase (cf. Fig. 3.6) alters the magnon dynamics, slowing down the process of thermalization and explaining the high recovery time observed in this phase. The SkL phase shows a more regular magnetic structure that can be pictured as follows: a uniform magnetic texture similar to a FM state with magnetic bubbles. The skyrmions, uniformly distributed in the FM background, as seen in Fig. 3.6. In regard to the magnon dynamics, skyrmions also act as magnetic defects and



scatter off the magnons slowing down the thermalization process. It must be considered that the more regular distribution of skyrmions and the overall magnetic order outside them provides a better environment for the diffusion of heat through magnons, hence explaining a recovery time lower than that in the Cyc phase, but still higher than the FM one. Finally, as the FM and paramagnetic (PM) phases do not show this kind of magnetic defects, the magnon dynamics are not altered. In fact the two phases show similar values of the recovery time.

In the next section we will introduce and describe the model that provides the theoretical framework on which our analysis is based.

### 3.3 The model

In the beginning of the previous section we described the properties and the structure of GVS. We stated that the magnetic properties of the material are due to the  $V_4$  tetrahedra and that, due to the lacunar spinels lacking every other A atom in the common spinel structure  $AB_2X_4$ , the  $V_4$  are not uniformly distributed but are arranged in larger and smaller tetrahedra. The V atoms are in different oxidation states; nominally a  $V_4$  tetrahedron contains three  $V^{3+}$  and one single  $V^{4+}$  and all the atoms hybridize to form a  $V_4$  cluster with a total spin of  $1/2$ .

We model the magnetic structure of GVS by considering the sublattice formed by  $V_4$  clusters. The effective spin-spin interaction is described with a semiclassical approach. While semiclassical treatment would not usually be justified for  $S = 1/2$ , GVS is long range ordered and the spin texture is locally ferromagnetic, which makes the effect of quantum fluctuations negligible. More detail is given in Section 3.4. We thus approximate our system with a classical Hamiltonian

$$\mathcal{H} = - \sum_{i,j} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j - \mathbf{D}_{ij} \mathbf{e}_i \times \mathbf{e}_j + K_i (\mathbf{e}_i \cdot \mathbf{n}_K)^2 - \mu_B \mathbf{B}^{ext} \cdot \mathbf{e}_i. \quad (3.4)$$

The Hamiltonian is written in terms of unitary vectors  $\mathbf{e}_i$  that represent the direction of the spin  $\mathbf{S}_i$  at site  $i$ .  $J_{ij}$  is the exchange coupling between in-plane or out-of-plane neighboring spins  $i$  and  $j$ ,  $\mathbf{D}_{ij}$  is the DM vector,  $K_i$  is the easy axis anisotropy constant related to the distortion along the direction  $\mathbf{n}_K$ , the  $[111]$  direction of the cubic lattice on which the  $V_4$  sit,  $\mathbf{B}^{ext}$  is the external magnetic field.

In order to describe the excitations and the time-dependent dynamics in GVS we make use of the Landau-Lifshitz-Gilbert (LLG) equation [45]:

$$\frac{d\mathbf{m}_i}{dt} = -\frac{\gamma}{1+\alpha^2} \mathbf{m}_i \times [\mathbf{B}_i + \mathbf{b}_i(t)] - \frac{\gamma}{m} \frac{\alpha}{1+\alpha^2} \mathbf{m}_i \times (\mathbf{m}_i \times [\mathbf{B}_i + \mathbf{b}_i(t)]). \quad (3.5)$$

The LLG equation describes the precessional motion of the magnetic moment  $\mathbf{m}_i$ , with modulus  $m$ , inside a material. In our case the magnetic moment is related to the total spin  $\mathbf{S}_i$  of the  $V_4$  cluster by the relation  $\mathbf{m}_i = g\mu_B/\hbar \mathbf{S}_i$ . The coefficient  $\gamma$  is the gyromagnetic ratio.  $\mathbf{b}_i(t)$  is a stochastic magnetic field that mimics the effect of finite temperature by introducing Gaussian fluctuations into the dynamics of the magnetization, which has the following properties

$$\langle b_{i\mu}(t) \rangle = 0, \quad \langle b_{i\mu}(t) b_{j\nu}(s) \rangle = 2D\delta_{\mu\nu}\delta_{ij}\delta(t-s), \quad (3.6)$$



where  $\langle \dots \rangle$  represents the time average,  $\mu$  and  $\nu$  select the Cartesian components of the vector  $\mathbf{b}_i(\mathbf{t})$ .  $\delta_{ij}$ ,  $\delta_{\mu\nu}$  are Kronecker deltas and  $\delta(t - s)$  is the Dirac delta.  $D$  is the amplitude of the stochastic field  $\mathbf{b}_i(\mathbf{t})$  [46]

$$D = \frac{\alpha}{1 + \alpha^2} \frac{k_B T}{\gamma m}. \quad (3.7)$$

and  $\alpha$  is a damping parameter. Finally  $\mathbf{B}_i$  is the effective magnetic field acting on the single magnetic moment  $\mathbf{m}_i$ , and responsible for the precessional motion of the magnetic moment. Its expression is obtained from the previously defined Hamiltonian (3.4),

$$\mathbf{B}_i = -\frac{\partial \mathcal{H}}{\partial \mathbf{m}_i} = -\frac{1}{m} \frac{\partial \mathcal{H}}{\partial \mathbf{e}_i}. \quad (3.8)$$

where in Hamiltonian (3.4)  $\mathbf{e}_i = \mathbf{m}_i/m$ . With Eqs. (3.4) and (3.5) we are able to model the real material. We begin by inserting experimental information such as interaction strength, geometry, symmetries etc. in Eq. (3.4). In particular, exchange coupling  $J$  and DM vectors  $\mathbf{D}_{ij}$  are taken from [47]. We then use the Hamiltonian to describe, for every spin, the effective magnetic field that produces the evolution of the system, and use the LLG equation to describe such evolution.

In the next section we show in detail the simulation we performed for GVS, highlight the commonalities and differences with the experimental data that we described in section 3.2.1, and discuss the results.

### 3.4 Simulations and results

In this section we report and discuss the results of our theoretical work and simulation for GVS. Our analysis makes use of the atomistic spin dynamics approach [48], that is implemented in the UppASD program [46]. It has been mentioned that the model which we base our study on is a classical one, even if the spins of the  $V_4$  tetrahedra have a total value of  $1/2$ . A classical model can be used in this case because of the particular spin texture of GVS. As the different magnetic orders are stabilized, the total order is reached on a long length scale compared to the single unit cell length (for example the periodicity of Cyc and SkL phase is of the order of 20 nm). This means that the change in magnetization is smooth through the cells, and that the spin direction varies slowly along the lattice resulting in short scale ferromagnetism that can be well described even with a classical model, such as the one implemented in the UppASD software [46].

Fig. 3.6(a-f) shows the simulated phases of GVS, the temperature in the simulation is different from the real material. We use the simulated phase diagram to rescale the temperature in the software to the equivalent real one. We present different snapshots of the simulated phase diagram at an equivalent temperature  $T = 12$  K. For each snapshot we plot the relative dispersion relations for magnons. The simulation successfully reproduces the phase diagram, as the magnetic field is increased a Cyc phase, a SkL phase and a FM phase are obtained. As we will discuss later on, there are some caveats about the aforementioned results. The finite size of the simulation cell, as well as the use of a classical model, causes a change in the value of the critical temperature and of the coupling with the external magnetic field. The temperatures and fields we report are rescaled to match the experimental observations.

Fig. 3.6(a'-f') shows the computed magnon branches that are crucial in the understanding of the thermal properties of GVS. The magnon branches are obtained from the magnon

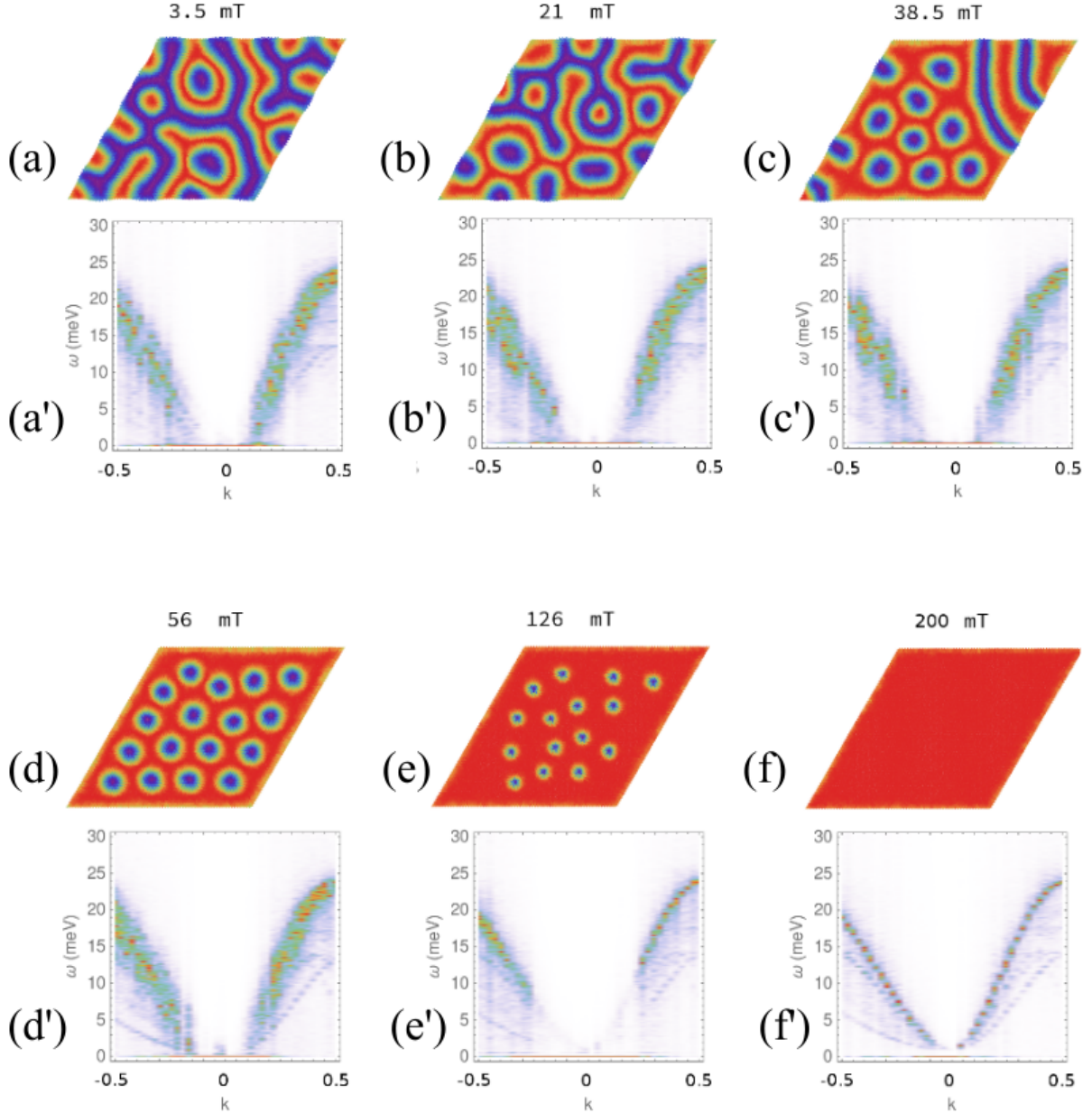


Figure 3.6: (a-d) Phase diagram simulated with UppASD for increasing values of the external magnetic field computed at an equivalent temperature of 12 K. A disordered spiral state is visible at the lowest magnetic fields. As the field increases the magnetic domains order and nucleate creating the magnetic texture typical of the SkL phase. Finally as the field further increases, the skyrmions become smaller until they disappear and the FM phase is reached. Color scale reflects the directions of spins, red are spin up and blue are spin down in the direction perpendicular to the page. (a'-d') Magnon spectral functions corresponding to top row phases. The more disordered the phase the broader the spectral function. The combination of disorder, and the presence of defects and magnetic DWs, results in the scattering of magnons, and hence introduces a change in their wave vector  $k$ . The smearing in the magnon branches is inversely proportional to the mean free path of the magnons. A lower mean free path results in a lower thermal conductivity, explaining the measurements of recovery time reported in Fig. 3.5. Color scale encodes the intensity of the spectrum.

spectral function. It is possible to compute this quantity through the time-dependent correlation function  $C^j(\mathbf{r} - \mathbf{r}', t)$  of the Cartesian component  $j$  of the magnetization  $\mathbf{m}_{\mathbf{r}}^j(t)$  at position  $\mathbf{r}$  and time  $t$ :

$$C^j(\mathbf{r} - \mathbf{r}', t) = \langle \mathbf{m}_{\mathbf{r}}^j(t) \mathbf{m}_{\mathbf{r}'}^j(0) \rangle - \langle \mathbf{m}_{\mathbf{r}}^j(t) \rangle \langle \mathbf{m}_{\mathbf{r}'}^j(0) \rangle, \quad (3.9)$$

whose Fourier transform gives the dynamical structure factor,  $S^j(\mathbf{q}, \omega)$ .

$$S^j(\mathbf{q}, \omega) = \frac{1}{\sqrt{2\pi}N} \sum_{\mathbf{r}, \mathbf{r}'} e^{-i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} \int_{-\infty}^{+\infty} e^{i\omega t} C^j(\mathbf{r} - \mathbf{r}', t) dt. \quad (3.10)$$

This quantity is directly computed by the software from the average values of the magnetization that have been sampled during the simulated time evolution. As we discussed in Section 3.2.1, the thermal conductivity changes considerably in the different phases. We see in Fig. 3.6 that the magnon branches for the different phases have similar shapes however the more “disordered” a phase appears, i.e. the farther is from the FM state, the broader the magnon branches are. The reason behind this broadening is due to the magnons scattering off the DWs or magnetic features that characterize the Cyc and SkL phases. The broadening is then inversely proportional to the magnon mean free path, that is approximately given by the distance between defects. The contribution of the single magnon to the thermal conductivity,  $\kappa_i$ , is given by

$$\kappa_i = c_i v_i \rho_i \quad (3.11)$$

where  $c_i$  is the specific heat of this particular magnon mode  $i$ ,  $v_i$  is the velocity and  $\rho_i$  is the mean free path of the magnon. The total thermal conductivity is the sum over all the channels that contribute to the heat transport. In this case it will be only over the magnons that are excited. In order for the magnetic order to affect the thermal conductivity of the system at least one of the quantities on the RHS of Eq. (3.11) must change. It is evident that only the mean free path of the magnon will be affected by the presence of magnetic DWs that are distributed in the Cyc or SkL phase and are absent in the FM phase. Thus the broadening of the magnon branches in  $k$ -space and the change of thermal conductivity are both consequences of the same scattering mechanism and the simulated broadening provides an indication for the experimentally observed thermal conductivity.

We now move to the study of the light-induced precession motion of the magnetization in GVS, as it is portrayed in Fig. 3.4. This particular task has been revealed to be quite challenging as the quenching mechanism induced by the laser excitation is not still fully understood. Our simulation provides a qualitative tool to support considerations on the quenching mechanism, but fails to exactly reproduce the experimental data. The reasons behind this discrepancy are diverse and will be discussed later.

The hypothesis we wanted to test is that the laser excitation triggers a quench of the anisotropy in GVS [35]: the laser would locally heat the material and change the geometric structure, a change that has repercussions for the anisotropy of the heated region. The spins precess to adjust to the new magnetic Hamiltonian: magnon modes are excited and are responsible for the change in the magnetization that is observed. In order to imitate this we manipulate the model parameters. We initialize the system with a set of physical quantities and let the magnetization evolve according to the LLG equation for a certain amount of time, then we change the anisotropy constant  $K_i$  in Eq. (3.4) to mimic the

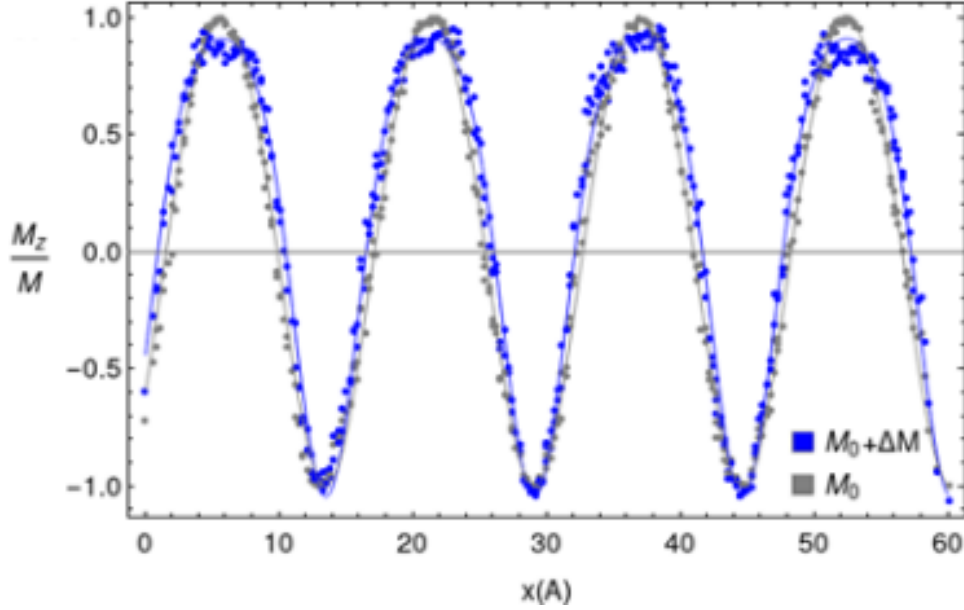


Figure 3.7: Photo-induced mode on the Cyc phase. Projection of the magnetization along the excited magnon mode before (grey) and after (blue) quenching. The excited mode slightly couples to the Cyc phase resulting in a weak decrease of the peaks of magnetization; the excited mode effectively “presses on” the spiral.

excitation and let the evolution proceed again. We simulated the response in the three phases, Cyc, SkL and FM (Figures 3.7, 3.8 and 3.9).

Figures 3.7 and 3.8 show the effect of the simulated quenching on the Cyc and the SkL phases. The effects on the FM phase are discussed later on. The response of the different phases to the excitation is qualitatively and quantitatively different. The laser photo-induced excitation has little effect on the Cyc phases; as Fig. 3.4 shows, the excitation amplitude in the Cyc phase (that is for the smallest external magnetic field) is smaller than in the SkL phase (around 50 mT in the figure).

It is not easy to see a change in the magnetic texture of the Cyc phase. In order to highlight it, we project the magnetization for the Cyc phase onto the main Fourier mode  $e^{(i\omega t)}$  before and after the quenching. We see only a small variation of the projected

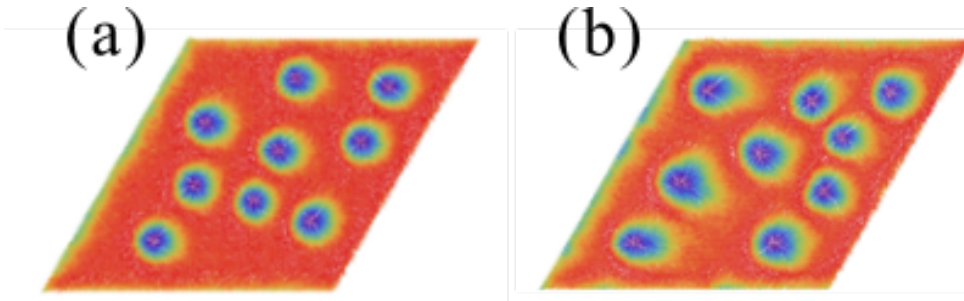


Figure 3.8: Breathing mode excitation in the SkL phase for (a) unquenched and (b) quenched SkL phase. The anisotropy is set in the plane for easier visualization of the effect of the mode. The skyrmions deform in the direction of the anisotropy, the excited mode is a breathing mode for the skyrmions. The color scale reflects the directions of spins, red are spin up and blue are spin down, in the direction perpendicular to the page.

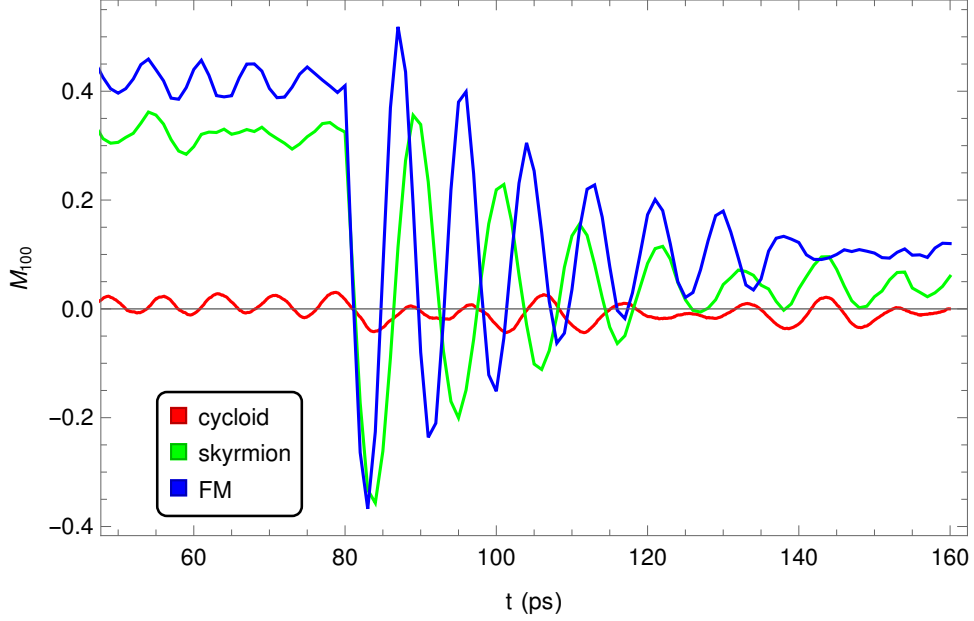


Figure 3.9: The simulated dynamics of the magnetization along [100] cubic direction in the three phases following the anisotropy quench. The anisotropy is quenched at 80 ps. The state was prepared using LLG dynamics with high Gilbert damping.

magnetization: the excited mode affects the Cyc phase by slightly “squashing” it, thus making the spiral more “square-shaped”. The measurements and the simulations show that the effect is minute, thus indicating small coupling of the excitation to the squashing mode. Magnetization oscillations are stronger in the SkL phase. Fig. 3.8 shows that skyrmions are significantly deformed by the excited mode and this is consistent with the higher oscillation amplitude of the magnetization in the SkL phase in Fig. 3.4.

The last part of our analysis concerns the coherent dynamics of magnons that we showed in Fig. 3.4. As we mentioned earlier our simulation does not reproduce the experimental results in their entirety but still provides valuable information that can help understand, or rule out, the proposed anisotropy quenching mechanism. Fig. 3.9 shows the simulated oscillation of the magnetization, projected on the direction of the magnetic field, that is the [100] direction of the cubic  $V_4$  lattice. To proceed we select one of the three magnetic phases (Cyc, SkL or FM) by setting the temperature and the external magnetic field to appropriate values according to the simulated phase diagram (Fig. 3.6) and let the system stabilize by evolving it under LLG dynamics, first with large damping, and then with regular damping.

At 80 ps we manually quenched the anisotropy of the system and we observe a strong response of the magnetization for FM and SkL phase, but only a small response in the Cyc phase. Comparing the simulation with the experimental plot we identify a number of inconsistencies:

- the oscillation frequency is not reproduced: the experimental oscillations are in the GHz range, while the simulated ones are of the THz range. In Fig. 3.4;
- the response of the FM phase is greatly different: in the simulated scenario the magnetization in the FM phase strongly oscillates after the quenching of the anisotropy, while the measured magnetization is hardly affected by the excitation;

- the oscillation in the Cyc phase is also quite different in the two cases: the overall shape is different, but simulation and experiments agree with the Cyc phase being weakly excited.

## 3.5 Conclusions

In this Chapter we have addressed recent experiments on the dependence of thermal conductivity in GVS on the magnetic phase. The decrease of the thermal conductivity in the SkL and especially Cyc phase is suggested to result from DWs scattering magnons, and thus reducing the magnon mean free path. We have also simulated the coherent oscillations of magnetization following the anisotropy quench, which was proposed earlier as the major effect of the photoexcitation on the magnetic subsystem. We also analyzed the result of anisotropy quench coherent magnetization precession have inconsistencies with the experiment, suggesting that anisotropy quench may not be the adequate way to mimic the photoexcitation. A solution could be related to the anisotropic  $g$ -factor, resulting from Jahn-Teller distortions. Heating may reduce the distortion amplitude, thus changing the  $g$ -tensor. We plan to test this hypothesis in a future work as the change in the  $g$ -tensor may be modelled, in our simulations, by a magnetic field rotation.